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SOUTHERN MARKETING
AND NUTRITION
RESEARCH DIVISION

AGRICULTURAL RESEARCH SERVICE • U.S. DEPARTMENT OF AGRICULTURE

PREFACE

This Technical Session was sponsored jointly by the Cane Sugar Refining Research Project, Inc., and the Southern Marketing and Nutrition Research Division of the Agricultural Research Service, USDA. The purpose of this biennial technical session is to report on research and recent developments in cane sugar refining and to provide for an interchange of information that will benefit future research and industry.

E. J. CULP, President
Cane Sugar Refining Research
Project, Inc.

C. H. FISHER, Director
Southern Marketing and Nutrition
Research Division

PROGRAM
Frank G. Carpenter

PROCEEDINGS
Margaret A. Clarke
Frank G. Carpenter

LOCAL ARRANGEMENTS
Robert L. Kelsey

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Underscored numbers in parentheses refer to references at the end of each paper. References, figures, and tables are reproduced essentially as they were supplied by the author of each paper.

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OPENING OF THE SESSION

by

E. J. CULP
Cane Sugar Refining Research Project, Inc.

I welcome you to the 1970 Technical Session on Cane Sugar Refining Research. This meeting is being sponsored jointly by the Cane Sugar Refining Research Project, Inc., and the Southern Marketing and Nutrition Research Division (SMNRD) of the Agricultural Research Service, USDA.

Fred R. Senti, Deputy Administrator of the Agricultural Research Service, Washington, D. C., and C. H. Fisher, Director of SMNRD, New Orleans, La., had hoped to be here. However, they have asked me to express their regrets at being unable to attend, and wish us all success in our meeting.

Before we get to the technical session, it is appropriate to report that our organization has made tremendous progress during the past 2 years, very largely through the leadership of Frank Carpenter. Frank is still at the helm and very active, as those of use who work with business affairs well know. The organization is in good shape.

Before starting the morning's proceedings, we should observe the place, date, and occasion. First, this is Columbus Day. Appropriately, our thoughts turn to historical items, and we remember that Boston is an important historical center. So while we are here, it is only fitting that those of us who have not done so, should go and see some of the historic shrines with which this city abounds. Also, Boston is on the fringe of our great area, New England, which is currently right at the height of the beautiful color foliage season. Those of you who can, should get out and look it over.

FIRST SESSION: George W. Muller, Jr., Kerr-McGee Chemical Corporation, Chairman

THE FUNCTION OF CHEMISORBED OXYGEN IN CARBON ADSORBENTS

by

Victor R. Deitz and J. L. Bitner
Naval Research Laboratory
Washington, D. C.

(Presented by Victor R. Deitz)

ABSTRACT

The noncarbon constituents (H, O, N, S) in carbon adsorbents, particularly oxygen, play a significant role in adsorption. In this study, the total oxygen contents of two carbon adsorbents were increased progressively by reaction with ozone at 26° C. Although each ozone-treated adsorbent gave evidence of continuous decomposition when introduced into a vacuum adsorption apparatus, stability was obtained when the sample was cooled to 77.4° K. Nitrogen adsorption isotherms were determined for samples at various stages of ozone treatment and after the outgassing of each sample at various temperatures. The ozone reaction resulted in products that had a considerably decreased nitrogen adsorption. Two explanations are examined. First, there could be a continuation of the etching reactions that prevailed during the formation of the original carbon adsorbent. This would lead to a structure having pores of greater diameter (and accordingly, less surface area) than the original charcoal. Second, there could be a blockage of the micropore openings to nitrogen molecules because of the chemisorption of oxygen at critical openings of the porous carbon structure. A sequence of three reactions is suggested to explain both the weight changes upon ozone treatment and the unique behavior of the nitrogen adsorption isotherm determined at 77.4° K.

INTRODUCTION

The formation of almost all commercial carbon adsorbents is accomplished by the pyrolysis of the organic source material and a "burn-off" in an oxidizing environment (O_2, CO, CO_2, H_2O). A deep etching of the carbonaceous residue takes place, which results in a large increase of surface area. As a result, oxygen is incorporated into the structure of the solid. This oxygen-containing state has been variously termed the "oxygen complex," "chemisorbed oxygen," "activated carbon complex," or "active carbon" (5). The principal elementary constituents include carbon, hydrogen, oxygen, nitrogen, and sulphur; the chemical bonding among all five elements is essentially covalent. Since the surface areas of carbon adsorbents (6) are quite large, a good working hypothesis is that the boundary surface may approach the overall chemical composition of the charcoal.

This study was undertaken in part to determine the effect of total oxygen content on the surface properties of carbon adsorbents. It may be possible, hopefully, to deduce from such information some structural features of the original charcoal. A convenient means to increase the oxygen content at room temperature is to treat the charcoal sample with a mixture of ozone and oxygen. The known reactions of ozone with carbon blacks (16), and of atomic oxygen in radio frequency discharges with polymer carbons and graphites (12, 13) furnish a good background for this study.

The results of these preliminary experiments with ozone are examined relative to some current researches on charcoal. The need to understand the structure of the carbon networks in charcoal is further intensified by the need to understand the nature of the chemical changes that take place on the introduction of oxygen into the extensive surface of a charcoal.

EXPERIMENTAL

The flow of dry oxygen (60 to 90 ml./min.) was directed into a laboratory ozone generator, then through the gas cell of a spectrophotometer, and over the charcoal samples, as shown in figure 1. Pyrex glassware, interchangeable ground joints, and Teflon tubing were used in construction of the apparatus. The concentration of ozone in oxygen was determined spectrophotometrically in a Beckman DU spectrophotometer using the Hartley Band at 2550 Å and a flow-through quartz cell of 10 mm. depth. The ozone concentration determined from the band maximum was quite steady over many hours of operation. The contour of the band agreed closely with the measurements of Inn and Tanaka (10).

The ozone concentrations could be varied from 0.2 to 5 percent (2,000 to 50,000 p.p.m.). The exit gases, after contact with the charcoal, were directed through a small bed of Hopcalite which completely destroyed the residual ozone. The flasks, which contained relatively small samples of charcoal, could be removed for weighing, analysis, etc.

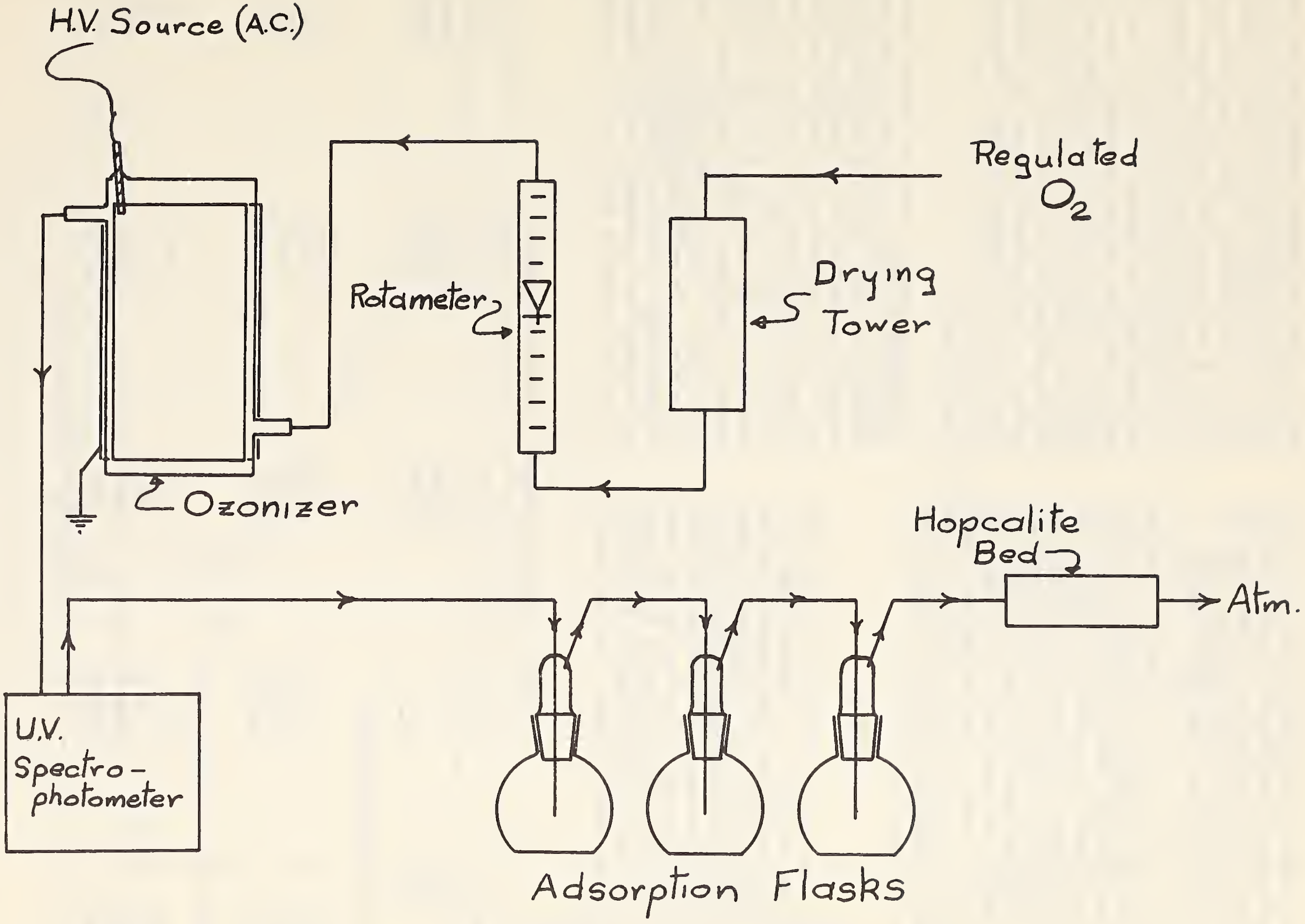

Figure 1. — Diagramatic sketch for ozone treatment of charcoals at room temperature.

Two samples of ash free charcoal were used, one an activated coconut shell charcoal, and the other an activated coal based charcoal. Both had been repeatedly treated with hydrochloric and hydrofluoric acids and then washed with a large volume of distilled water.

Samples of the original and ozone treated charcoals were analyzed for carbon and hydrogen; in view of the very small sulfur and nitrogen content ($<$0.1 percent), the oxygen could be estimated by difference. The vacuum outgassing of the sample was interrupted at regular intervals by isolating the sample container and measuring the pressure buildup. In addition, the pressures were also determined in a known volume, with a cold finger either at room temperature, in liquid nitrogen, or in solid carbon dioxide slush. The adsorption isotherms of nitrogen for the samples were determined volumetrically at 77.4° K.

RESULTS

The weight changes of the coconut charcoal during ozone treatment at 26° C. are shown in figure 2. A similar curve was obtained upon ozonation of the coal based charcoal. There was an immediate, significant increase in weight, which passed through a maximum and then slowly decreased. In contrast, previous studies with carbon blacks (16) in ozone reported only weight losses. The elementary analyses of the charcoals, however, showed a continuous decrease in carbon and a continuous increase in oxygen. The results given in table 1 are for the original charcoal and the ozone treated products sampled at positions A, B, and C of figure 2. A high oxygen content in the ozone treated product is compatible with a highly disordered carbon network in the charcoal. This was first pointed out by Watt and Franklin (23), who compared the oxidation of a polyvinylidene chloride char by ozone at room temperature with the oxidation by oxygen at 300° to 450° C. The large increase in hydrogen cannot be explained at present, since a long exposure to dry oxygen and ozone should have minimized its presence. The present uncertainty as to the source and form of binding of the hydrogen prevents any definitive interpretation of the present data. The accumulation of hydrogen in the charcoal during ozone treatment is to be studied further.

Outgassing behavior. — When an ozonized charcoal was evacuated in preparation for the gas adsorption studies, it was found that the pressure buildup when the sample was isolated from the pumps was too rapid even at room temperature to permit volumetric adsorption measurements. The gases evolved were mainly carbon dioxide, carbon monoxide, and smaller quantities of water vapor (1, 2, 11, 16). This rapid evolution of gas indicated a large loss in weight of the sample upon evacuation, large enough to raise uncertainties in the weight and the composition of the adsorbent sample. In order to establish the magnitude of the weight loss on heating, a sample of ozonized charcoal was followed by T.G.A. in a flow of nitrogen

Table 1. — Elementary analyses of ozone-treated charcoals

Sample	Exposure	Carbon	Hydrogen	Oxygen
	Min.	Weight percent	Weight percent	Weight percent
Series II coconut shell charcoal:				
Original	—	94.1	0.52	5.4
Point A	1365	78.3	3.46	18.2
Point B	9560	54.2	3.60	42.2
Point C	18100	45.7	3.94	50.3
Series III coal base charcoal:				
Original	—	94.2	0.9	4.9
Point A	313	88.8	1.8	9.4
Point B	2670	59.3	2.4	38.3
Point C	6805	53.0	2.8	44.2

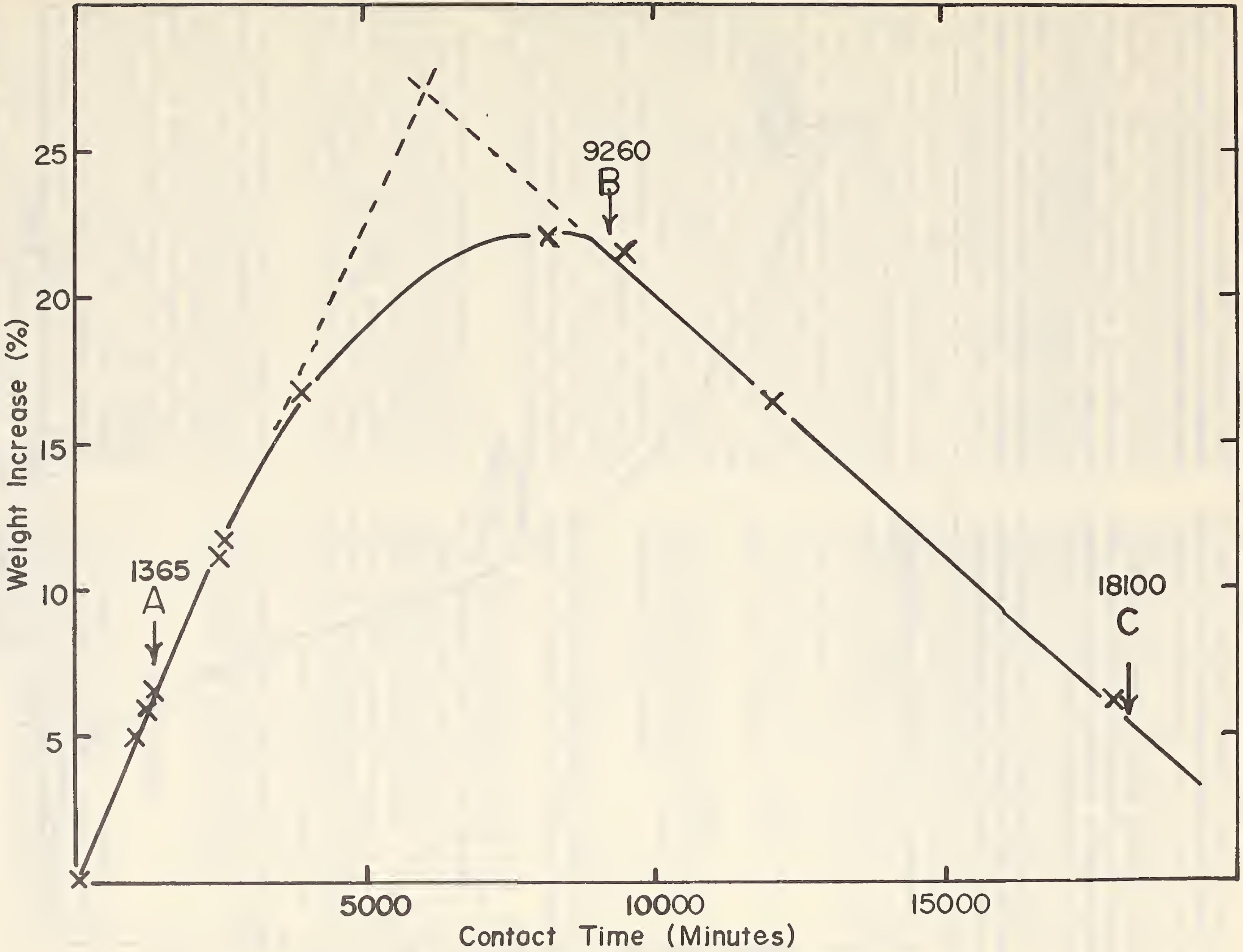

Figure 2. — Weight changes observed in the ozone treatment of coconut charcoal at 26° C. Samples removed for study at times designated at A, B, and C.

(83 ml./min.) with a constant temperature gradient of 1° C./min. The results presented in figure 3 are for a coal based charcoal that had been sampled at point B of figure 2 (17.6 percent weight increase). The weight loss was continuous during the time of observation and there was no indication that a steady state weight might be realized in the range of temperature explored. After 6 hours the weight had decreased by 33 percent.

Fortunately, the evolution of gases from an ozone treated charcoal was found to decrease to practically zero when the sample was cooled with liquid nitrogen. The following experimental procedure was thus feasible: (1) a given charcoal can be reacted with ozone to increase the oxygen content by a specified amount, (2) the sample can then be evacuated for a specified time and temperature to modify further the composition of the charcoal, (3) the sample can then be cooled to 77.4° K. with liquid nitrogen. A study can now be made of the adsorption of the residual oxygen contents of the charcoal. In this study, nitrogen adsorption isotherms were determined for charcoals at selected stages of ozone treatment and at selected intervals in the outgassing program. In each

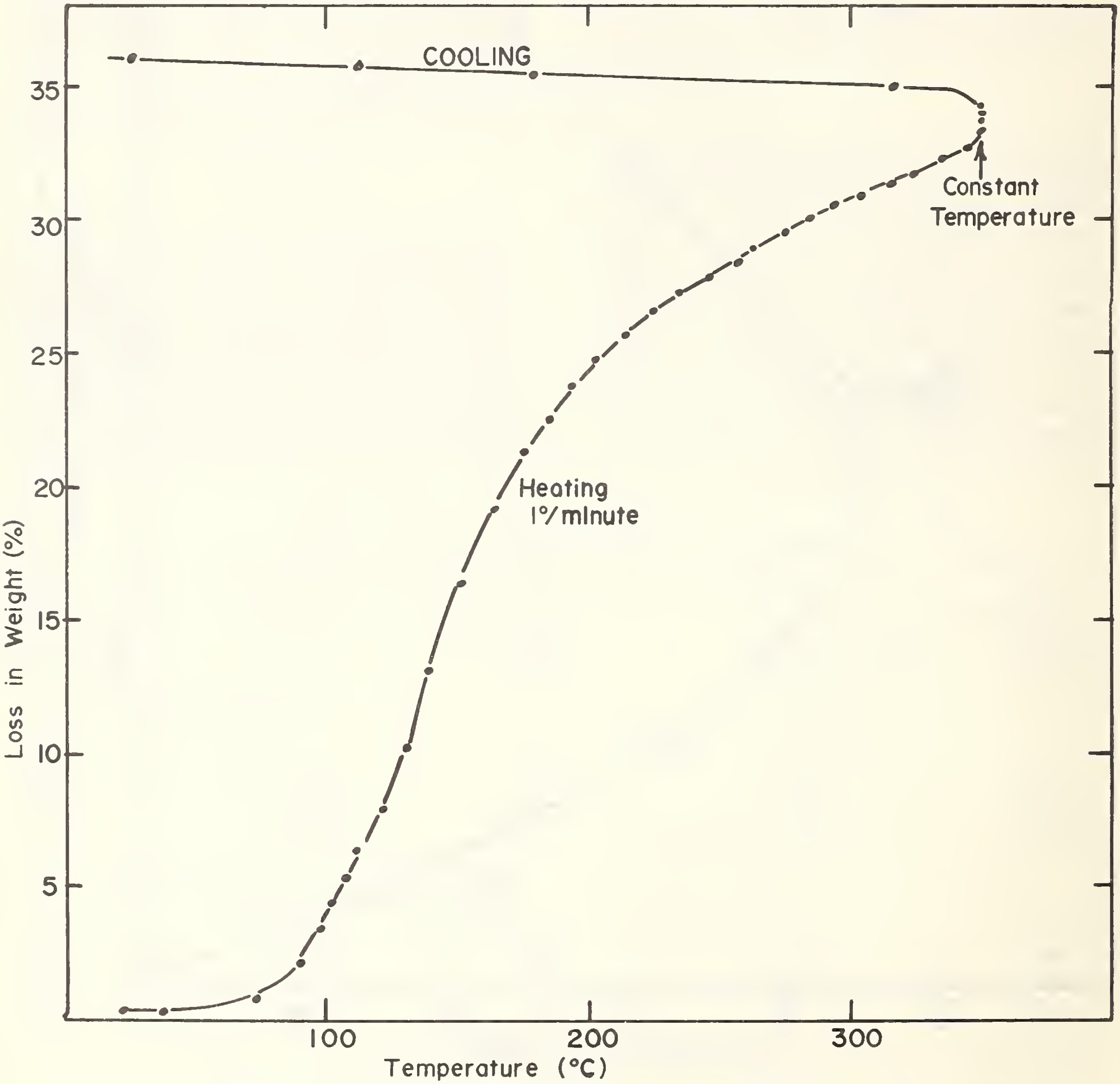

Figure 3. — Loss in weight upon heating ozone-treated coconut charcoal in nitrogen (83 ml./min.) in a constant gradient of 1°C. per minute.

case, the weight of the sample and the analysis for carbon and hydrogen were determined after the nitrogen adsorption measurements had been completed and the samples returned to room temperature in nitrogen.

Nitrogen adsorption at 77.4° K. — The adsorption of nitrogen on the original coconut shell charcoal is shown at the top of figure 4. The BET plots were not linear and an estimate of monolayer coverage, determined by the point B-method (4), was 16,000 micromoles per gram of outgassed material.

The ozone treated charcoal sampled at point A (7 weight percent increase) was evacuated at 98° C. for 1,000 minutes, cooled to 77.4° K., and the nitrogen isotherm determined. The sample was subsequently heated for 1,000 minutes at 228° C., cooled to 77.4° K., and the nitrogen adsorption again determined. The isotherms for the two outgassed samples given in figure 4 are slightly below that for the original charcoal, but in general, all three have the same shape and magnitude. Although the sample at point A had increased in weight by about 7 percent, it lost this on outgassing. Thus, it might appear possible to recover the adsorption characteristics of the original charcoal after an ozone treatment to this level. However, a chemical analysis of the outgassed ozone treated charcoal showed that its oxygen content had decreased from 18.2 (see table 1) to 14.4 percent by weight. This is still considerably above the oxygen content of the original charcoal and demonstrates the permanent change brought about by ozone.

Using an area for monolayer coverage of 1,500 m^2 per gram and a cross-sectional area of 10 Å^2 for the chemisorbed oxygen atom, it can be estimated that a monolayer coverage of oxygen would correspond to a weight increase of 25 weight percent. Therefore, approximately one third of the available charcoal surface is statistically involved when the sample is ozonized up to point A.

The product sampled at point B (22 weight percent increase) was evacuated progressively at 26.7°, 125°, and 230° C. After each heating the nitrogen adsorption was determined at 77.4° K. The isotherms are given in figure 5. As with the charcoal samples at point A, a progressive loss in weight occurred with an increase in the temperature of outgassing, and the nitrogen adsorbed per unit weight of outgassed material decreased in the same sequence. Moreover, hysteresis was observed, as seen in figure 5, for all three outgassed samples, with no indication of loop closure at the lowest observed desorption pressure. A significant change is that the adsorption had decreased to approximately one-third that of the untreated sample, and a less-sharp knee is shown in the adsorption isotherms.

The final sample obtained at point C (7 weight percent increase), has a completely different adsorption behavior as shown in figure 6. The sequential evacuation was at 26.8°, 119°, and 230° C., and the corresponding weight loss during desorption increased to 52 weight percent at the highest temperatures. The magnitude of adsorption is about 1/20th that of the original charcoal, and the pronounced hysteresis shows no indication of closure at the lowest desorption pressure. In contrast to the samples obtained at A and B, the nitrogen adsorption now increased in the same sequence as weight loss. It may be noted in figure 6 that the adsorption isotherm after degassing at 230° C. is nearly linear. This is not common behavior in physical adsorption of nitrogen at 77.4° K.

The new findings of the ozone reaction with charcoal may be summarized as follows:

1. There is a sequence of weight gain followed by weight loss during the ozone treatment which makes any interpretation of adsorptive properties on a unit weight basis quite incomplete.

2. There are changes in the composition of the treated charcoals that progressively increase the oxygen content and, unexpectedly, the hydrogen content.

3. There are complicated changes in nitrogen adsorption at 77.4° K that vary with the extent of the ozone treatment and with the intensity of the outgassing treatment (time and temperature) given each sample before the measurements at 77.4° K. These include (1) small changes in adsorption when sampled at stage A, (2) some decrease at stage B, and (3) large decrease at the C stage of ozonization. There is some recovery of nitrogen adsorption by the C sample after desorption at progressively higher temperatures.

4. The surprisingly large increase in the hydrogen content during ozone treatment cannot be explained, but will be made the subject of further study.

DISCUSSION

One characteristic property of an adsorbent charcoal is its extensive micropore structure. This is so designated because the adsorbed gas has to enter into the porous structure through slit-like openings not much larger than the molecular dimensions of the adsorbed molecule.

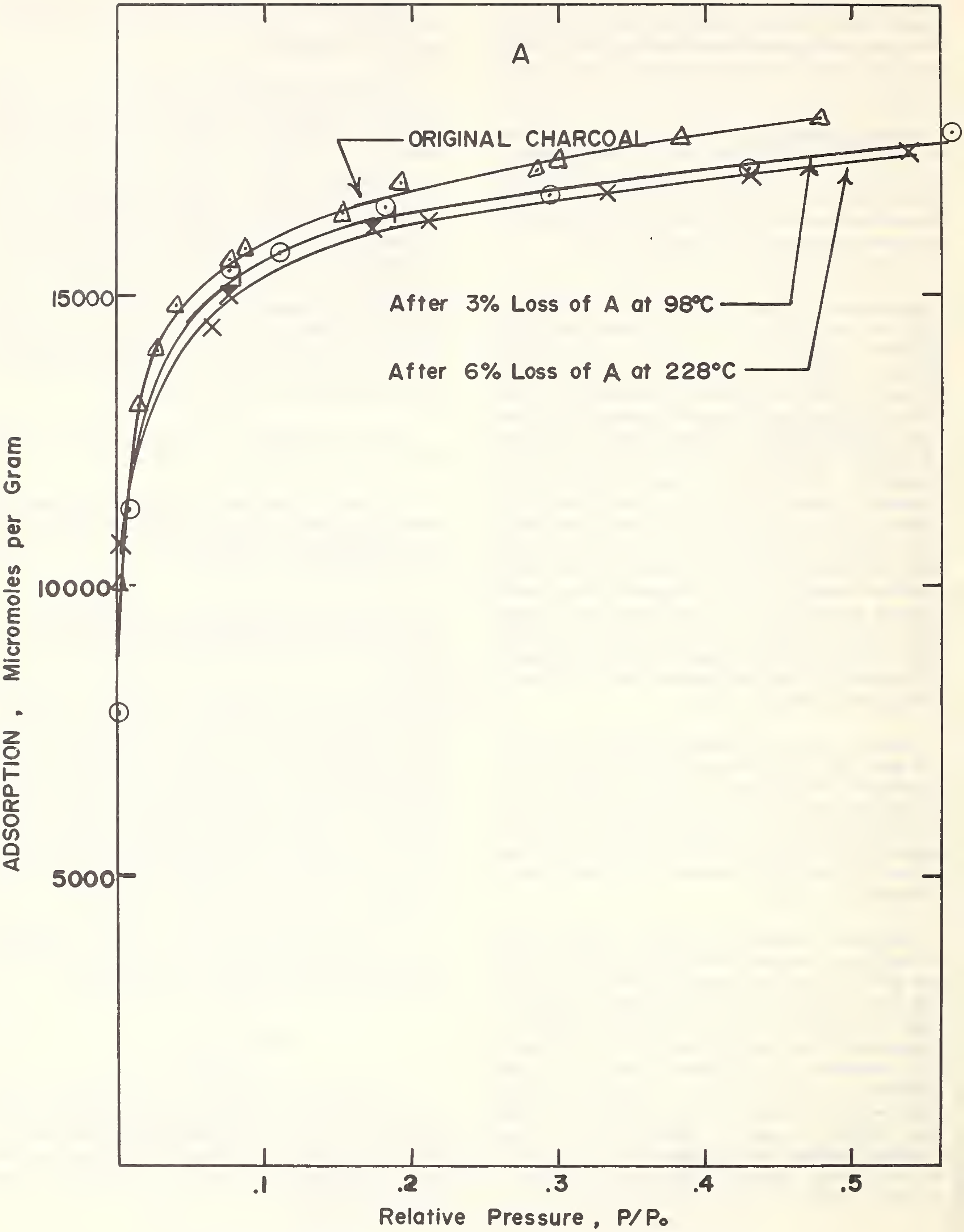

Figure 4. — Nitrogen adsorption (77.4° K) by ozone-treated coconut charcoal sampled at point A of figure 2.

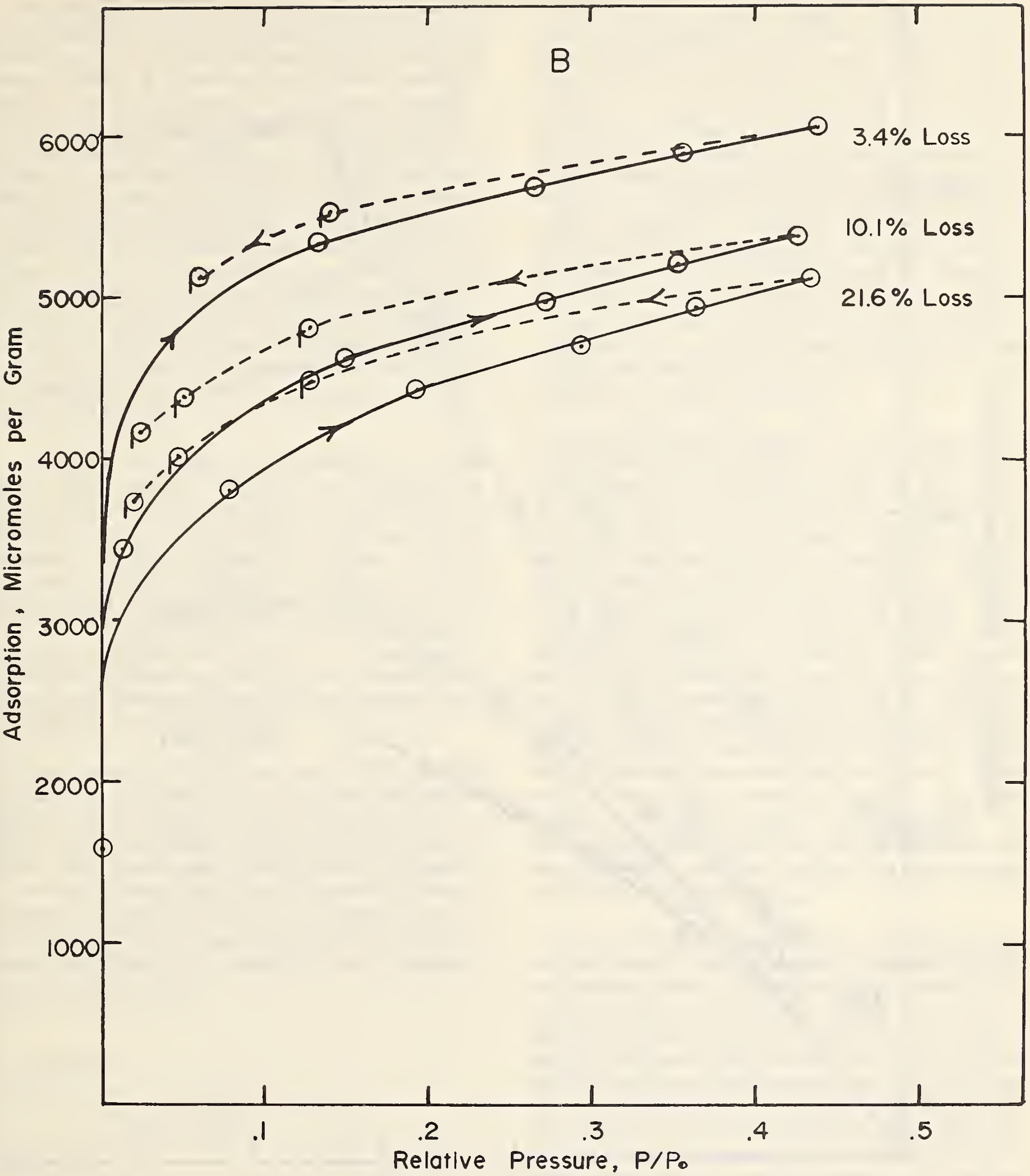

Figure 5. — Nitrogen adsorption (77.4° K) by ozone-treated charcoal sampled at point B of figure 2. (3.4 percent loss at 26.7° C., 10.1 percent loss at 125° C., and 21.6 percent loss at 230° C.)

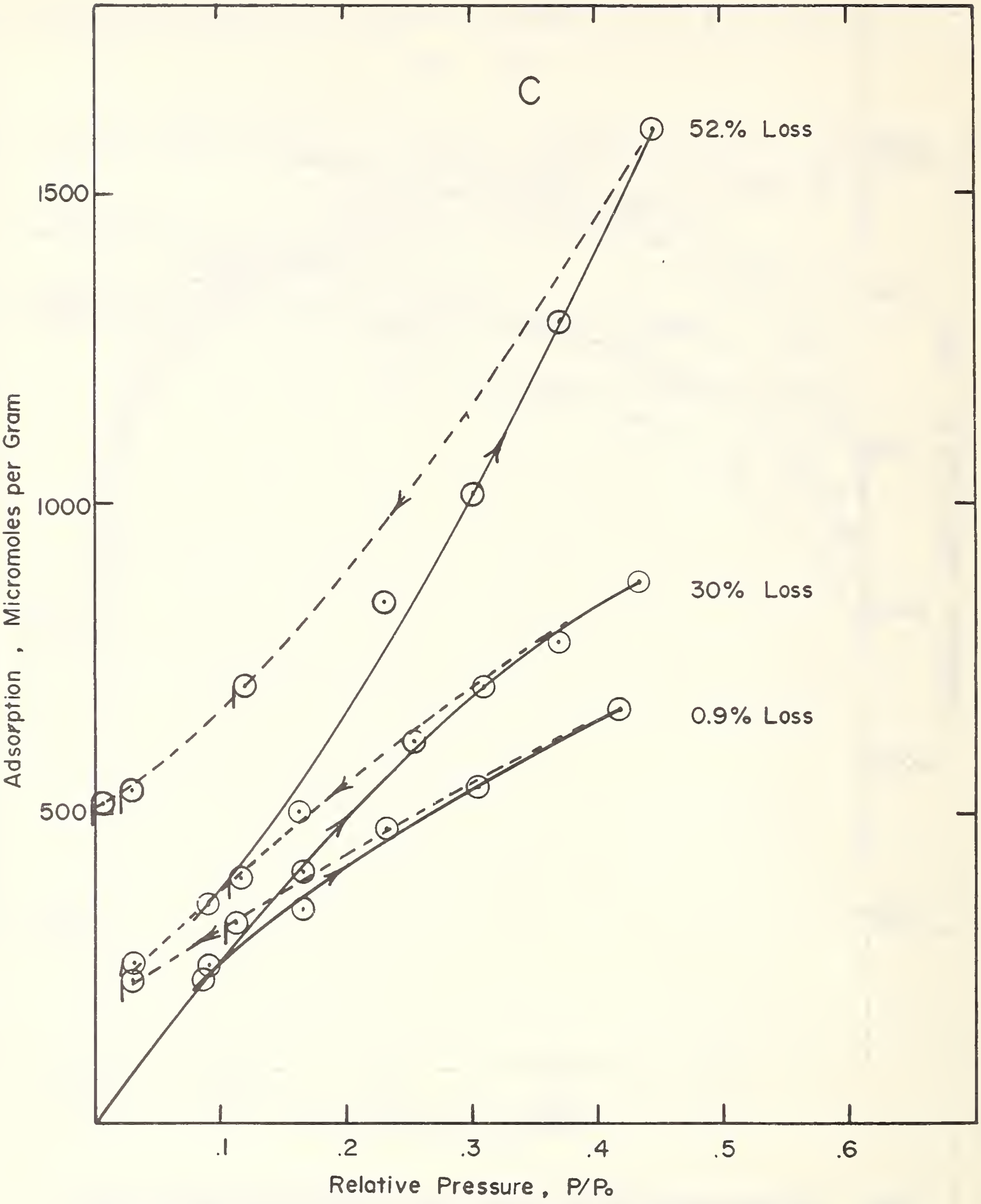

Figure 6. — Nitrogen adsorption (77.4° K) by ozone-treated charcoal sampled at point C of figure 2. (0.9 percent loss at 26.8° C., 30 percent loss at 119° C., and 52 percent loss at 230° C.)

The reaction of ozone with the original charcoal can be considered to occur in several stages. At the beginning, the oxidation reactions can pit or etch the charcoal surface in a manner similar to the "burn-off" reactions in the formation of the carbon adsorbent. This etching process would increase the surface area, i.e. the nitrogen adsorption. A second stage of oxidation could then follow and gasify the walls that are a part of the porous structure. When this occurs, the surface area should decrease. A different course of ozone reactivity could lead to the chemisorption of an oxygen atom at the narrow openings of the microporous structure of the original charcoal. Thus, the access of molecules into the micropore would be blocked. The observed decrease in nitrogen adsorption would be due either to the progressive removal of the wall structure, the micropore plugging, or both, by chemisorbed oxygen.

A decision between these alternatives could be made, based on the adsorption of molecules of different molecular cross section. Charcoal is known (21) to show a molecular-sieve effect due to the exclusion of large adsorbate molecules by the micropore openings. Progressive etching by ozone could enlarge the openings and reduce any steric influence on the adsorption process. However, if micropore plugging takes place to an appreciable extent, the molecular-sieve effect would become more critical than with the original charcoal. Measurements are in process to test this model.

Three reactions of ozone with charcoal are suggested as a guide for future experimentation. Should micropore plugging by the chemisorption of an oxygen atom take place, surface reactions of type I (below) may predominate with minimum production of carbon dioxide and carbon monoxide. Should progressive etching take place, surface reactions II and III would become more important. Reaction II leads to minor weight changes and reaction III to continuous major weight decreases.

$$C_xO_y\text{(solid)} + O_3 \rightarrow C_xO_{y-1}\text{(solid)} + O_2 \qquad \text{I}$$

$$C_xO_y\text{(solid)} + O_3 \rightarrow C_{x-1}O_{y+1}\text{(solid)} + CO_2 \qquad \text{II}$$

$$C_xO_y\text{(solid)} + O_3 \rightarrow C_{x-2}O_y\text{(solid)} + CO_2 + CO \qquad \text{III}$$

The maximum weight changes shown in figure 2 may be explained by the relative extents to which these reactions take place. Current studies are in progress to determine the quantities of CO and CO_2 produced at various contact times in order to determine the extents of reactions I, II, and III. In the reaction of ozone with carbon black (Spheron 6), Papirer, Donnet, and Schutz (16) reported only carbon dioxide as a volatile product. In the gases evolved on heating samples of ozonized charcoal, we have observed both carbon monoxide and carbon dioxide, the former in quantities much larger than anticipated. Marsh, O'Hair, and Wynne-Jones (12) also reported both gases in heating polyvinylidene chloride carbon progressively from room temperature to 900° C: their carbon had been subjected to reaction with atomic oxygen in a microwave discharge.

Surface functional groups — The interactions that are reponsible for adsorption are due not only to the polarizability of the adsorbate molecules, but also to the polarizability of constituents of the surface, such as oxygen. Since the total oxygen content can now be increased manyfold and can be subsequently modified, it is pertinent to examine the variety of chemical bonds that can be formed. Functional groups which have been detected at carbon surfaces by direct chemical means (3, 22) include the ketone, alcohol, and carboxyl groups. The presence of other groups may be inferred from behavior in aqueous media, for example, acid anhydrides from pH measurements. The difference between total oxygen concentration and the oxygen content in the above functional groups may be considerable. The remaining oxygen has been designated as "ether oxygen", i.e. —C—O—C—. The absolute quantities of any of these groups have not been established, since the chemical reactions involved are not without ambiguity (17).

In the past, infrared absorption measurements have not been helpful because carbons are basically opaque to infrared radiation. Using the "temperamental" KBr pellet technique, Deitz[1] observed the presence of absorption bands at 3500 and 1620 $cm.^{-1}$ in coconut charcoal and bone char. These bands were not present with FT graphitized carbon black observed under the same conditions. However, the two bands are close to the 3415 and 1640 $cm.^{-1}$ bands of silica which are definitely due to adsorbed water vapor. Therefore, the above bands may be caused by water in the charcoal samples. Recently, Friedel and Hafer, also using KBr pellets (7), have shown the presence of 1735, 1590, and 1215 $cm.^{-1}$ bands after very intense grinding of charcoal. These were interpreted as due to carbonyl, aromatic structures, or unconjugated chelated carbonyl, and —C—O— groups. However, intensive grinding has been shown by Savage (18, 19) and Gregg and Hickman (8) to lead to chemical changes of the parent carbon, which raises a question as to the interpretation of Friedel and Hafer.

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[1] Deitz, V. R. 1963. Unpublished work of the Bone Char Research Project at the National Bureau of Standards.

Smith, Young and Smith (20) obtained absorption peaks when they reacted ozone at 25° C. with thin films of hydrogen free carbon made from the pyrolysis of carbon suboxide. A strong band was reported at 1745 $cm.^{-1}$ and very weak bands at 1562 and 1351 $cm.^{-1}$. The strong band was ascribed to the carbonyl stretching frequency resulting from the surface reaction: $-C + O_3 \rightarrow -C{=}O + O_2$.

Infrared internal reflectance spectroscopy has been recently applied by Mattson and Mark (14, 15) in the study of surface functional groups in active carbons. Bands at 1710—1750 and 1750—1770 $cm.^{-1}$ were ascribed to significant amounts of carbonyl and carboxyl groups. The bands in the region 1510—1625 $cm.^{-1}$, ascribed to C=O bonds, are strongly variable and need much detailed work in order to follow the influence of pretreatment, i.e. both environment and temperature. An ether type linkage —C—O—C— would give a broad band at 1140—1230 $cm.^{-1}$. Such a linkage could produce a type of micropore plugging of exceptional thermal stability. The bands at 1140—1230 $cm.^{-1}$, however, have not been observed on graphites or carbon blacks. The band positions are summarized below. One can conclude that the complete gamut of oxygen-containing functional groups may be present in charcoals.

Infrared Band Positions by Internal Reflectance in an Activated Sugar Carbon (14)

1140 to 1230 $cm.^{-1}$	(300° to 700°C.) —C—C— or —C—O—C—
1590 to 1625 $cm.^{-1}$	carbonyl and
1510 to 1560 $cm.^{-1}$	carboxyl
1710 to 1770 $cm.^{-1}$	anhydrides of carboxylic acids

This vastly complicates the identification of those groups that participate in the adsorption of organic molecules from either gas phase or solution. In addition, it is probable that unstable groups, such as peroxides and ozonides (9), are formed among the ozone reaction products.

An important fundamental problem is the reversibility of the oxidation reactions. Loebenstein and Deitz (11) showed that oxygen adsorbed at 200° C. by charcoal could be in part desorbed as O_2 by heating to 400° C. There is also some evidence that residual ozone is present when a mixture of ozone and oxygen is circulated in a closed system through charcoal for long periods. If evidence for reversibility of ozone adsorption is found, some understanding may be forthcoming of the experimental conditions for realizing reversible oxygen-carbon electrode reactions.

Current applications — Since oxygen is the major noncarbon constituent in carbon adsorbents, it is the oxygen-containing functional groups which have received most attention (3). This is relevant to several current applications, such as the activation of a charcoal and the development of an adsorbent of very large specific surface area. In granular carbon adsorbents, an added complication is the need to maintain the required hardness and abrasion resistance of the granules. Several questions may be raised: (1) Is it possible chemically to increase the adsorption per unit area by introducing reactive groups in the boundary surface? (2) In the development of the elaborate fine-grained porosity of a carbon adsorbent, are there accompanying changes in the surface composition of the wall structure that are significant to the adsorption process? It is desirable to have an adsorbent 50 to 100 percent better than current material and even more desirable to realize a more uniform product on a granule-to-granule basis. These questions require that more attention be given to the chemical composition of the adsorbing surface.

When a granular adsorbent is to be regenerated, there are particular requirements that need not exist for adsorbents that will be used only once. The porosity should entail a wider pore size distribution, which is desirable for a rapid ingress and exit of gases. It is also necessary to maintain granule hardness and abrasion resistance in order to withstand the rigors of material handling in the regeneration process. A limited reaction with ozone can modify the charcoal so that changes in the pore size distribution may occur.

The regeneration of finely divided carbon adsorbents is presently of great importance. The reactivity of hot air dried water slurries of carbon is well known to be difficult to control. How to modify the heat transfer characteristics and avoid run-away reactions is a major consideration. The reaction with ozone at ambient temperatures is worth considering as a means of selective oxidation of the adsorbed impurity. Some fundamental knowledge of this reaction, as well as those with oxygen containing gases, is singularly lacking.

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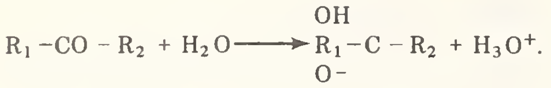
DISCUSSION

F. M. WILLIAMS: Would you care to comment on the role oxygen plays in causing the acid reaction in carbon; that is, the reduction in pH in the treatment of sugar liquors?

V. R. DEITZ: It has been known for some time that the acidic or basic character of a carbon adsorbent depends on its history of formation and, particularly, upon the temperature and environment in which it has been heated. In regard to the application of granular carbons to sugar refining this must, therefore, include the kiln used to regenerate the material. One mechanism for a lower pH of the effluent is the formation of an acid anhydride grouping during kilning. Chemical addition of water to the regenerated carbon could yield the acidic carboxylic groups:

$$R_1-CO-O-CO-R_2 + H_2O \longrightarrow R_1COOH + R_2COOH.$$

A second mechanism is a surface hydrolysis of the oxygen containing complex. The resultant group containing OH must remain in the chemisorbed product(s) and the acidic group dissolves in the sugar liquor:



$$R_1-CO-R_2 + H_2O \longrightarrow R_1-\underset{O^-}{\overset{OH}{C}}-R_2 + H_3O^+.$$

Peroxide and similar higher oxidized complexes can also ionize in water to yield extracts of acidic pH. I. M. Kolthoff (1935. Jour. Amer. Chem. Soc. 54: 4473-4480) was the first investigator in this country to recognize the acidic and alkaline properties of charcoals. The European literature had reported this earlier, inasmuch as the starting materials were of various ranks of coal. The detailed surface structure of any adsorbent carbon is unknown; instead, the appeal is made by analogy with the principles of organic chemistry. The validity of applying specific reactions of organic chemistry to the identification and estimation of surface groups on carbon can be questioned.

One conclusion of the paper just presented was to demonstrate that oxygen can be incorporated into the network of a carbonaceous residue with no contribution to the adsorbent properties. The model here is the formation of the nonreactive ether linkage characteristic of some polymers.

S. B. SMITH: You've mentioned the extent of oxygen present on the surface. Could you give any idea of what percentage of the total carbon surface area might be tied up in these oxygenated groups?

V. R. DEITZ: The surface composition may be estimated from two knowns: the surface area of the carbon, and a complete chemical analysis. It is necessary to assume that the mole fraction of each component of the solid extends into the surface. This assumption has good validity for carbons of large surface area and known amorphous structure. Knowing the covalent radius of oxygen, the mole fraction of oxygen, and the total surface area, it is possible to calculate the fractional oxygen coverage. The results indicate that it is possible to increase the surface fraction of oxygen from 2.5 percent for an acid-washed commercial coconut shell charcoal to 25 percent for the ozone-treated product.

The limited thermal stability of the product necessitates an important precaution in experimental work. We once passed ozone from a swimming-pool ozone generator through a 3-inch diameter column of a granular charcoal with the complete removal of the ozone. As the days went by, one could see the line of demarcation between the grey coloration of the product and the black coloration of the original charcoal. Then one day the column exploded, fortunately with no one present. As a result, the present experimentation is done with samples of no more than 100 milligrams. In order to protect the adsorption apparatus we have included a coarse fritted glass filter between the sample space and the rest of the apparatus. This serves as a barrier, should the sample become unstable. The detonated dust is still very high in oxygen content.

G. W. MULLER, JR.: At what temperature did the spontaneous combustions or blow-ups take place?

V. R. DEITZ: We were heating the carbon to outgas it and in one experiment had reached about 350° C. when the small sample detonated.

T. M. RINEHART: Do you think we could achieve these treatments by adding something to the wash water?

V. R. DEITZ: Experience to date has not been successful in doing so. We use anhydrous conditions: dry ozone and charcoal that has been dried at 105° C.

L. A. ANHAISER: During regeneration, is there any real danger of producing any toxic compounds, such as carbon monoxide?

V. R. DEITZ: All of our ozone-treated samples slowly evolve carbon monoxide. This can be shown with the aid of a small commercial carbon monoxide detecting tube. The air is drawn through the charcoal and then through the detector tube by a hand-operated squeeze pump. Using some materials that were several months old, the color characteristic of carbon monoxide readily formed, indicating about 300 to 400 p.p.m. CO.

C. C. CHOU: What was the sample designated "FT"?

V. R. DEITZ: The FT carbon black was produced by the Cabot Corporation and it had been graphitized. It was obtained from Walter Smith as one of several research grade carbon blacks.

C. C. CHOU: Would you care to comment on the active site on the carbon — whether it is due to the π-electrons or broken edge? If it is due to the π-electrons, what would be the effect of the electron-donating group and electron-withdrawing group in the adsorption process?

V. R. DEITZ: The commercial carbon adsorbent is the product of a series of thermal decompositions involving complex chain reactions in which the free radicals produced react with undissociated organic structures. This is followed generally by a controlled burning process during which activation and the characteristic large surface area of adsorbent carbon are developed. The two alternatives that Dr. Chou gives for the origin of "the active site on the carbon" are a vast oversimplification of the problem.

Present knowledge concerning oxidations that produce free radicals has been summarized by W. A. Waters (Chem. Phys. Carbon 6: 125 (1970)): (1) The ease of radical formation by attack on an organic matrix follows the order of the redox potential of the oxidizing agent; (2) the organic molecules most prone to attack have unshared electrons available, i.e., on $-\overset{\bullet\bullet}{\underset{\bullet\bullet}{O}}-$, $=\overset{\bullet\bullet}{N}-$, or $-\overset{\bullet\bullet}{\underset{\bullet\bullet}{S}}-$ atoms; π-electrons of double bonds in olefins are more easily removed than the shared electrons of σ bonds; (3) the ease of one-electron removal from an organic molecule depends on the degree of resonance stabilization of the resultant free radical.

The structure of the charcoal itself is poorly known and there is uncertainty that the graphitic crystallites assumed by Franklin in her pioneering work on carbon solids are truly present in amorphous structures.

B. G. LOUROS: You commented on the effect of oxygen on the micropore. Would you care to comment on any influence of chemisorbed oxygen on the macropore activity?

V. R. DEITZ: Blocking the entrance into the micropore structure would result in a decrease in the adsorption of small molecules like water and sucrose. The influence of ozone on the geometry of the macropore structure would be small. As a result, sucrose and water retention by the washed charcoal would be decreased. No experimental work in this direction has as yet been undertaken.

SOME ASPECTS OF THE PORE STRUCTURE OF CARBONACEOUS ADSORBENTS

by

Chung Chi Chou
Amstar Corporation
Brooklyn, N. Y.

ABSTRACT

Low temperature nitrogen adsorption studies, adsorption from aqueous solution, and oxidation studies were used to examine the pore structure of carbonaceous adsorbents. An activated condition is required for the entry of an adsorbate molecule into the "ink bottle" type pore. The "activated entry" effect is used to explain the mechanism of sucrose retention which is largely a pore filling process. Pore blockage accounts for the deterioration of adsorbents during service.

INTRODUCTION

The pore structure of carbonaceous adsorbents is of interest to both the adsorbent manufacturer and to the sugar refiner. In the adsorbent manufacturing process, measurements of the pore volume and pore size distribution can be used to follow the physical structural changes and to control the adsorptive characteristic of the adsorbents. In sugar refining, these parameters are essential for the study of the effect of operational variables on the efficiency of the adsorption process.

Most of the previous work on this subject was devoted to the study of the pore volume and pore size distribution of the adsorbents. Investigation into the pore shape of the adsorbents has received less attention. In the present work, several techniques, such as low temperature nitrogen sorption, adsorption from solution, and oxidation studies were employed to investigate the pore shape, specifically the ink bottle type pore of the adsorbents. The practical significance of the ink bottle type pore in the adsorption process is presented. An example of the application of the study of the "activated entry" effect is also given.

EXPERIMENTAL METHODS

Nitrogen sorption isotherm. — The nitrogen sorption isotherms were measured at a temperature of -195° C. using an Isorpta Analyzer Model 2 made by Englehard Industries, Inc.; Newark, N. J.

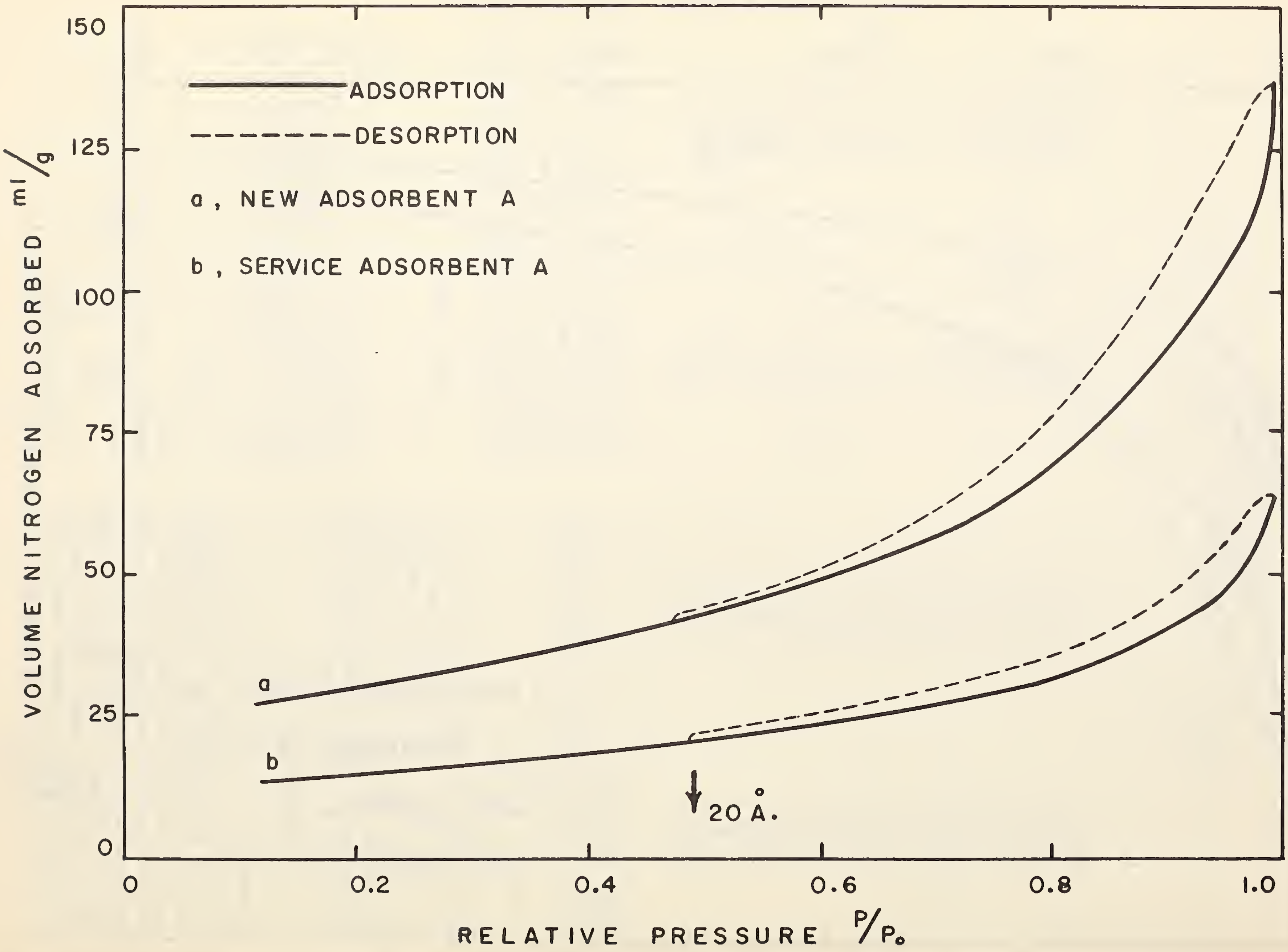
Adsorption of Cetyl Trimethyl Ammonium Bromide (CTAB). — The equilibration of the CTAB solution with the adsorbents was carried out in sealed glass tubes containing 10 ml. of solution and 0.2 to 0.25 g. of new adsorbent or 0.45 to 0.5 g. of service adsorbent. The glass tubes were rotated in an end-over-end shaker for 16 hours in either a water bath at 32° C. or in an air bath at 75° C. depending on the system. The difference in the concentration of CTAB solution before and after equilibration was used to calculate the amount of CTAB sorbed.

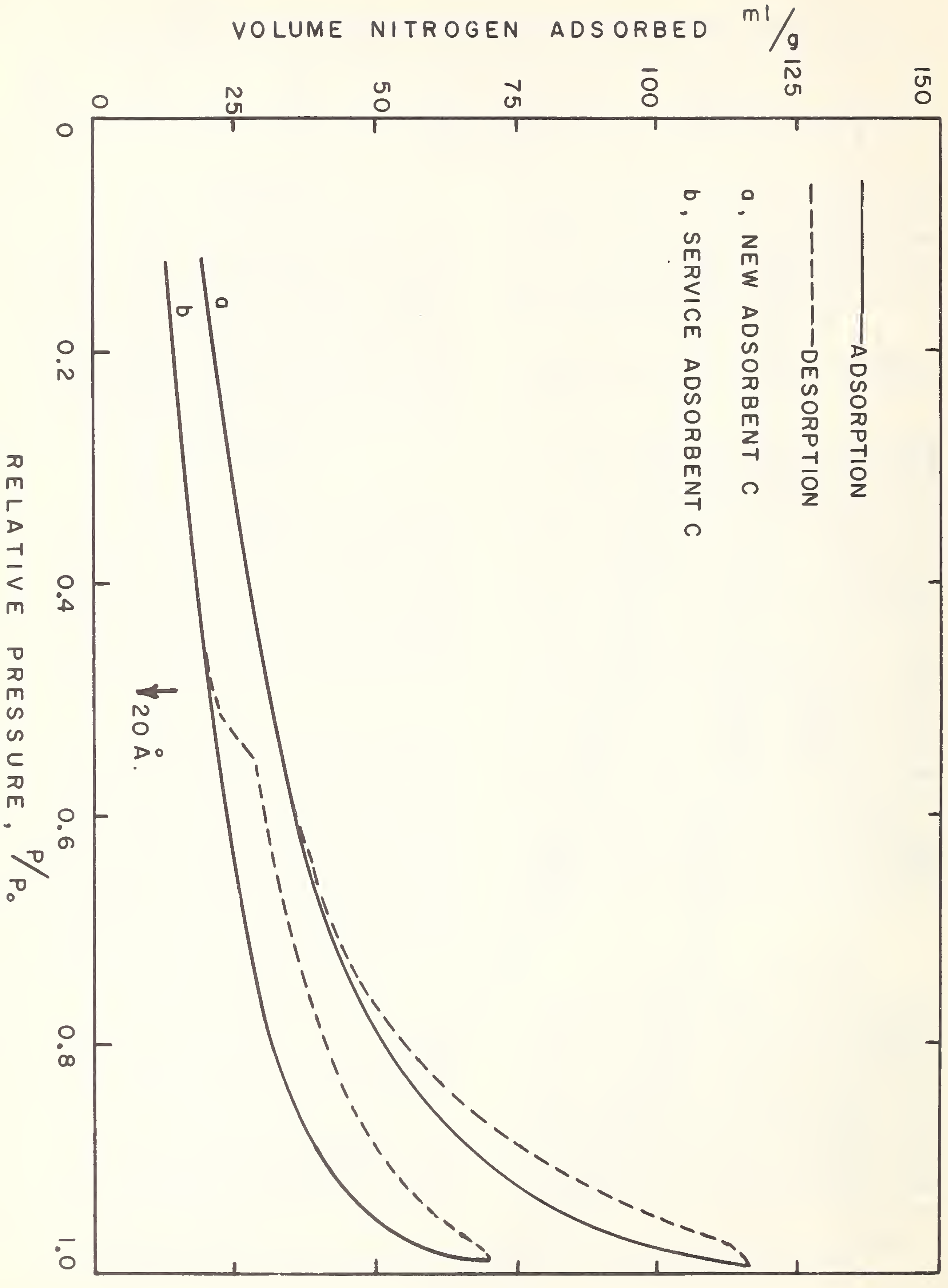
Oxidation study. — The detailed procedure for the oxidation of carbon of adsorbents was described elsewhere (5).

Retention of sucrose on adsorbents. — The retention tests were done in sealed glass tubes, each containing 10 ml. of 60° Brix, tagged pure sucrose solution and 2 g. of the adsorbent. The glass tubes were rotated in an end-over-end shaker for 16 hours in an air bath at 30° or 75° C., depending on the system. After decanting, the adsorbents were collected on a filter pad and washed to displace the maximum amount of liquor. The adsorbents were then transferred to small columns 5/8 inch in diameter and 6 inches in height. The adsorbents were then washed for 48 hours with water at 30° or 75° C., depending on the system. The water was delivered by a Technicon proportioning pump at a flow rate of 0.4 ml. per minute. During the washing, the water levels in the columns were 3 inches above the adsorbent surfaces. After washing, the adsorbents were dried and ground for radioactivity measurements. The sucrose retention on adsorbents was calculated from the specific activity of the sucrose solution and the unit activity of the washed adsorbents. In the radioactivity measurements, the number of counts in each measurement was so taken that the deviation in 95 percent of the determinations did not exceed 2.0 percent.

RESULTS AND DISCUSSION

Nitrogen sorption isotherms. — Typical sorption isotherms of various adsorbents, chosen to illustrate the effect of repeated use and reactivation, are shown in figures 1 and 2. The solid lines show the adsorption isotherms, and the dotted lines represent the desorption isotherms. An interesting finding is that a hysteresis loop in the adsorption-desorption cycle is observed for all the adsorbents tested, implying that the sorption process occurs irreversibly. Several possible causes of sorption hysteresis have been suggested (3), such as impurities on the adsorbent


ADSORPTION
DESORPTION
a, NEW ADSORBENT A
b, SERVICE ADSORBENT A
VOLUME NITROGEN ADSORBED ml/g
150
125
100
75
50
25
0
a
b
20 Å.
0
0.2
0.4
0.6
0.8
1.0
RELATIVE PRESSURE P/P₀


VOLUME NITROGEN ADSORBED ml/g
0
25
50
75
100
125
150
RELATIVE PRESSURE, P/P₀
0
0.2
0.4
0.6
0.8
1.0
ADSORPTION
DESORPTION
a, NEW ADSORBENT C
b, SERVICE ADSORBENT C
a
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20 Å.

surface (10), the presence of some irreversible sorbate phase change (2), and irreversible swelling of the sorbent. However, in general, the observation of reproducible isotherm hysteresis may be associated with the presence of a certain type of pore in the adsorbents. Since we are dealing with capillary condensation in the nitrogen sorption process, the occurrence of hysteresis may be interpreted by examining the pore geometry of the adsorbents together with the mechanism of condensation and evaporation.

(1) Cohan's open pore hypothesis:

The discussion of Cohan's theory (6, 7) may be facilitated with the diagrams presented in figure 3. The hysteresis was explained in terms of the differences in shapes of the meniscus: hemispherical in desorption, and cylindrical in the early stages of adsorption. According to Cohan, for a capillary with open end and radius r, condensation (adsorption) will take place at a pressure of

$$P_a = P_o \exp\left(\frac{-\sigma V}{rRT}\right) .$$

However, the pressure at which evaporation (desorption) will occur must be calculated from the classical Kelvin equation,

$$P_d = P_o \exp\left(\frac{-2\sigma V}{rRT}\right) ,$$

if zero contact angle is assumed. From the above equation, P_a and P_d are related by the simple equation,

$$P_a^2 = P_d P_o,$$

where P_a is the pressure on the adsorption and P_d is that on the desorption branch for a given amount adsorbed. Experimentally, this relationship is not found, suggesting that the open pore hypothesis can not be readily used to explain the observed hysteresis in the system studied.

(2) Ink bottle theory:

The "bottle neck" theory was initially suggested by Kraemer (8) and subsequently modified by McBain (9). According to this hypothesis, the pores contain constrictions with radius r_1 at the narrow neck and r_2 at the wide section as shown in figure 4. On the adsorption branch the vapor pressure is in equilibrium with the meniscus in the wider part of the body of the

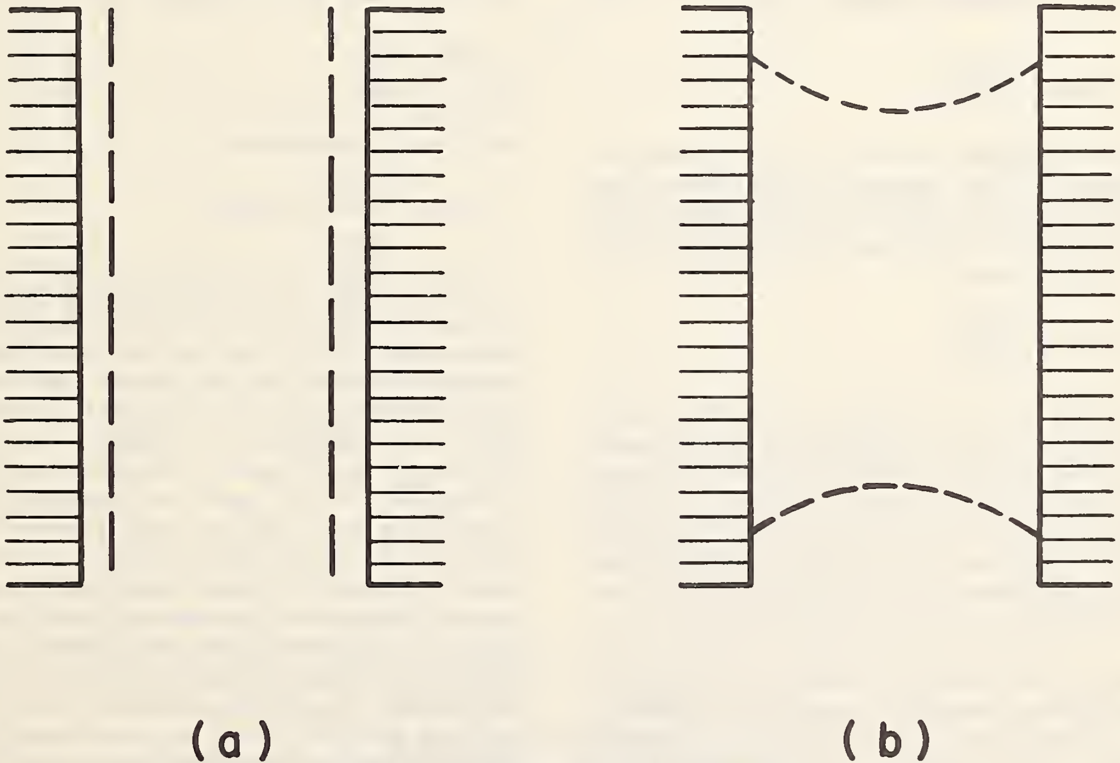

Figure 3. — Cohan's theory for hysteresis:
(a) cylindrical meniscus.
(b) hemispherical meniscus.

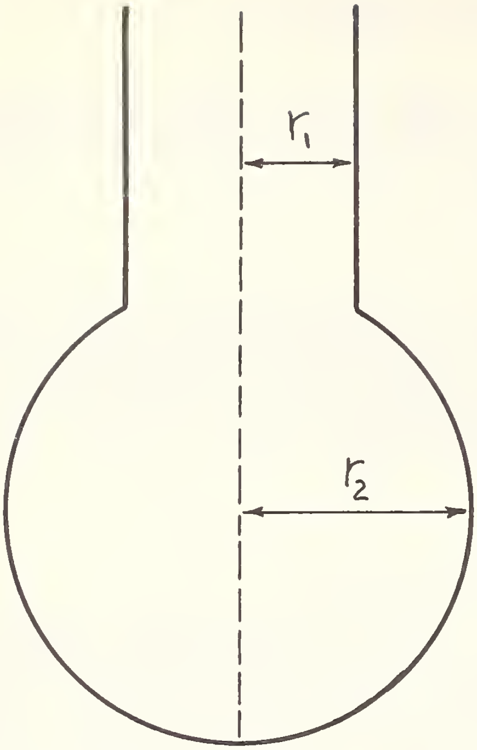

Figure 4. — "Ink bottle" type pore.

pore. Condensation in the body of the pore will take place when the pressure reaches the value

$$\frac{P_2}{Po} = \exp\left(\frac{-2\sigma V}{r_2 RT}\right) .$$

On the desorption branch, the vapor pressure is in equilibrium with the meniscus near the bottle neck. Therefore, the evaporation from the pore body can not occur at pressure P_2. The pore remains filled until the vapor pressure reaches

$$\frac{P_2}{Po} = \exp\left(\frac{-2\sigma V}{r_1 RT}\right)$$

corresponding to the constriction radius. The pore is then emptied at once. According to this argument, condensation along the adsorption branch occurs at a higher relative pressure than evaporation along the desorption branch for a given quantity adsorbed. It might be pointed out that according to this hypothesis, the adsorption process more nearly approaches the true state of equilibrium than the desorption process.

However, since the relative pressure, which is related to the chemical potential by the simple formulation, $\mu = \mu^\circ + RT\ln p$, or $\mu = \mu^\circ + RT\ln f$ (in the terms of fugacity), is lower along the desorption branch, it is conceivable that the desorption process is more likely to correspond to a state of equilibrium. It is to be noted that when the system is in a state of equilibrium, the chemical potential of the adsorbates in the adsorbed state must be equal to that of the adsorbates in the vapor phase.

On the basis of the argument presented, it may be concluded that the adsorbents examined contain a proportion of ink bottle type pores.

Adsorption from solution. — Further support of the presence of ink bottle type pores in the adsorbents is provided by a study of the temperature effect of CTAB sorption onto the adsorbents from aqueous solution. The method is based on thermodynamic consideration of the adsorption process. The free energy change in an adsorption process is given by the equation

$$\Delta F = \Delta H - T \Delta S$$

In the system studied, it appears that the entropy of the system tends to decrease upon adsorption of an adsorbate onto the adsorbent surface. Therefore, the entropy change ΔS is negative and the term $-T \Delta S$ must be positive. It is immediately obvious that for the free energy of the system to decrease, the change in enthalpy must be negative. That is, the adsorption process is exothermic. Based on the van't Hoff and Arrhenius law, the equilibrium constant K of a system can be expressed by the equation

$$\frac{d\ln K}{dt} = \frac{\Delta H}{RT^2}$$

The equation integrates to

$$\ln K = \frac{-\Delta H}{RT} + \text{constant.}$$

Since enthalpy ΔH is negative, it is obvious that adsorption should decrease with increasing temperature. This is the case for most adsorption processes. However, for some systems, particularly for porous adsorbents, physical adsorption often increases with rise in temperature. An explanation of this kind of anomaly can be given in terms of the effect of constriction. If the pores of adsorbents contain constrictions which are only slightly larger than the dimension of the adsorbate molecules, the molecules must be activated in order to pass constrictions. This type of adsorption is considered to be an "activated" process. Each molecule must pass an energy barrier of height, E, in order to enter the ink bottle type pore. The number of molecules entering the cavity can be given by $Ae^{-E/RT}$, where A is a constant which is usually known as the frequency factor for the reaction. The factor $e^{-E/RT}$ is recognized as the Boltzman expression for the fraction of molecules having energy in excess of the value E, so that it may be identified with the fraction of molecules that would gain entry into the cavity. Since E is positive, the magnitude of $e^{-E/RT}$ will increase exponentially with rise in temperature, so that the measured adsorption will increase correspondingly as temperature increases. According to this picture, the presence of an "activated entry" effect, that is, adsorption increase with rise in temperature, can be taken as an indication of the presence of the ink bottle type pore in adsorbents. It must be re-emphasized that the statement is valid only when the system is in a state of equilibrium. This is illustrated in figure 5, which is for ordinary adsorption without constrictions, "activated entry", or ink bottle type pores. This figure clearly demonstrates that, while the equilibrium adsorption decreases with increasing temperature, the rate of adsorption increases with rise in temperature. If equilibrium is not reached, an increase in temperature may lead to an increase in adsorption. This may be due to the fact that the rate now becomes appreciable, rather than to the presence of the ink bottle type pore in adsorbents.

On the basis of the above arguments, it is possible to study the presence of ink bottle type pores in adsorbents, using adsorption from solution at two different temperatures. Since the sorption of CTAB onto the carbonaceous adsorbent's surface has been studied to a great extent (1, 4), it is chosen as the adsorbate in this study. Accordingly, the sorption of CTAB on various adsorbents was determined at temperatures of 32° and 75° C. The results are shown in table 1. The sorption obtained at 75° C. is termed as "activated" sorption as deduced from the previously

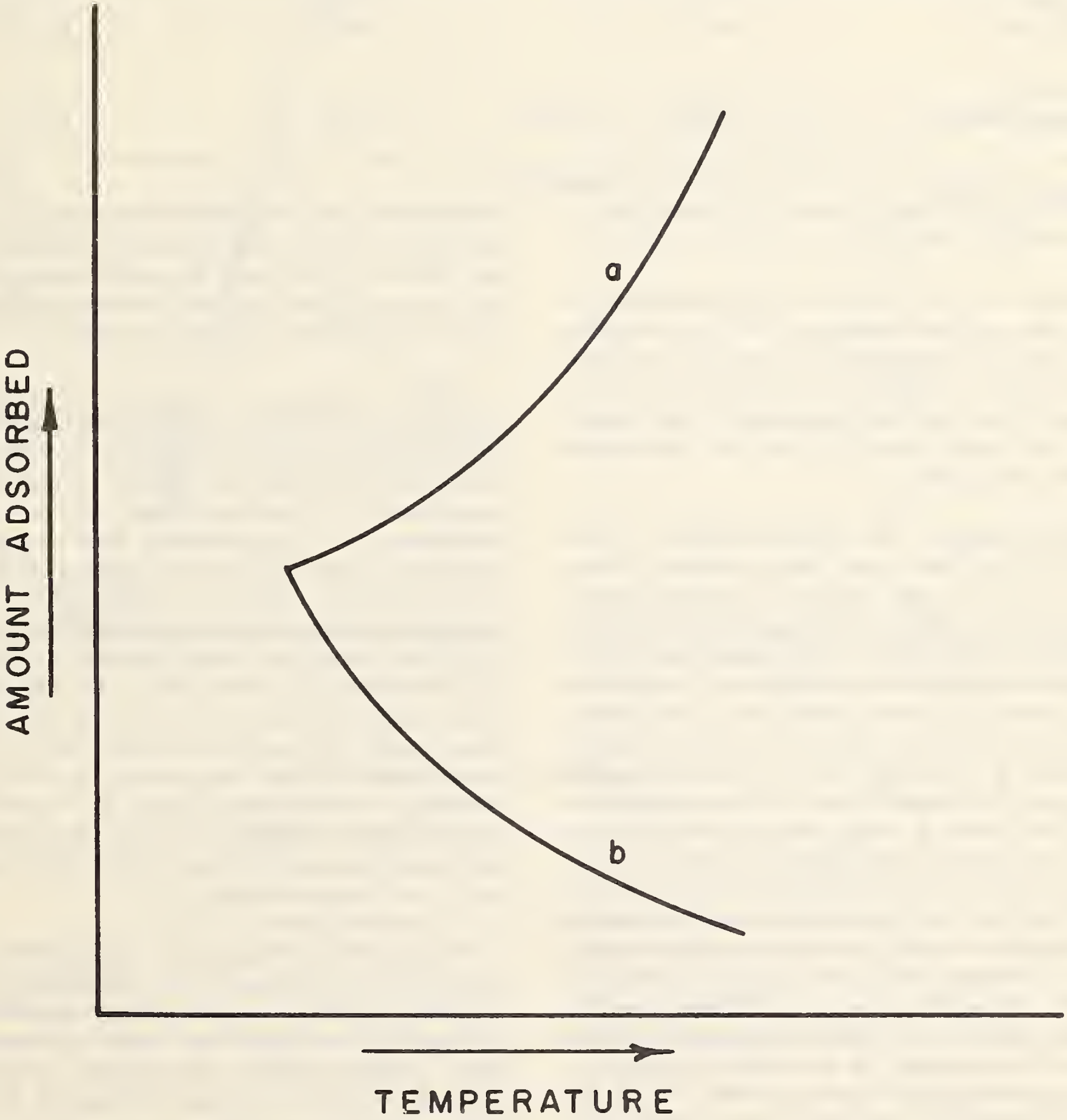

Figure 5. — Schematic adsorption isobar showing the effect of temperature on (a) the rate of adsorption, and (b) the equilibrium adsorption.

Table 1. — The effect of temperature on CTAB sorption by adsorbents

Samples	Sorption of CTAB at 32° C. µmoles/g. adsorbent	Sorption of CTAB at 75° C. µmoles/g. adsorbent	Percent of activated entry
New adsorbent A	228.3	235.8	3.2
Service adsorbent A	62.3	72.5	14.1
New adsorbent B	148.3	195.8	24.3
Service adsorbent B	43.0	46.4	7.3
New adsorbent C	156.2	209.0	25.3
Service adsorbent C	44.9	79.6	43.6

described "activated entry" effect. The percentage of "activated entry" is also given.

Examination of the data shows that the sorption of CTAB at the activated condition (75° C.) is higher than that at a temperature of 32° C. for the adsorbents studied, indicating the presence of the ink bottle type pore in the adsorbents. The results confirmed the earlier finding by the low temperature nitrogen sorption technique.

Oxidation studies. — The oxidation study of the carbon of the adsorbent also furnished some information on the pore structure of the adsorbent. Figure 6 shows the effect of time and temperature on the oxidation of the carbon of the adsorbent. For the sample studied, the total carbon burned off leveled out after 15 minutes. The total weight loss at the plateau of curves is taken as the maximum accessible carbon. As indicated in figure 6, the maximum accessible carbon is seen to increase with a rise in temperature, implying that there is some carbon which can be oxidized only at a high temperature. The result may be explained in terms of the "activated entry" of oxygen molecules into the ink bottle type pores which have a "neck" diameter of about the same magnitude as that of oxygen molecules. This "activated entry" effect also controls for the reaction product to diffuse out of the ink bottle type pores. This investigation provides evidence of the existence of ink bottle type pores in the micropore region, in agreement with the general conclusion arrived at by two other independent methods. It must be pointed out that the disappearance of the hysteresis loops below a radius of about 20 Å (figs. 1 and 2) does not necessarily imply the absence of ink bottle type pores below this region, but rather is due to the limited applicability of Kelvin's hypothesis in a micropore region.

Mechanism of sucrose retention by adsorbent. — One of the many possible applications of the "activated entry" effect is in studying the mechanism of sucrose retention by an adsorbent. Two mechanisms of sorption from solution are well recognized in a liquid-porous solid system: surface adsorption is generally used to describe the adsorption of adsorbates onto a solid surface, including chemisorption and physical adsorption; alternatively, a pore filling model has been suggested for the sorption of adsorbates by porous solids. In the pore filling theory, the pore volume of a solid influences, to a great extent, the sorption characteristic of the system under consideration. The theory is still open to criticism. For the present study, the "pore filling" is defined as the "trapping" of sucrose molecules into the ink bottle type pores. This is obviously a special case of a pore filling mechanism.

The retention of sugar on a service char at various experimental conditions was determined by the previously described method and the results are shown in table 2. The results can easily be interpreted in terms of the activated entry theory discussed under nitrogen adsorption. It has been shown in previous sections that the adsorbent possesses certain ink bottle type pores which are considered capable of trapping an

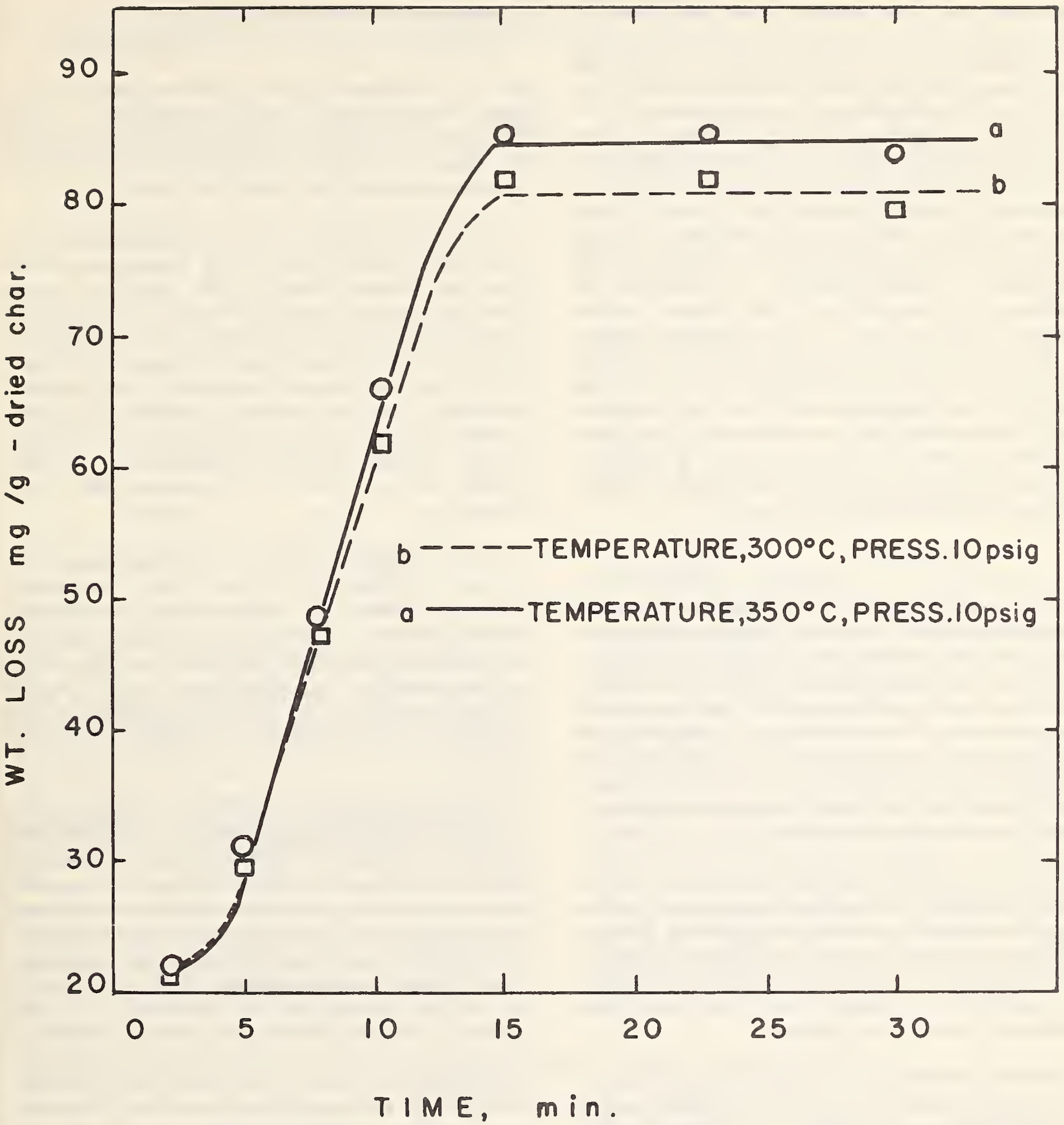

Figure 6. — Effect of temperature on the maximum accessible carbon.

Table 2. — Sucrose retention of a service char at various conditions

Experiment designation	Sorption temperature	Washing temperature	Sucrose retention
	° C.	° C.	Percent on char
a	30	30	0.45
b	75	75	.63
c	30	75	.20
d	75	30	1.28

appreciable amount of sucrose. As discussed previously, the sucrose molecule has to be activated, i.e., the kinetic energy of the molecule increased by raising the temperature, in order to enter or diffuse out of the ink bottle type pores. During the sorption process at 75° C., the sucrose molecule is relatively highly activated and enters the ink bottle type pore. If the adsorbent is then washed with water at a temperature of 30° C., a considerable amount of sucrose will be retained inside the pore because of the low kinetic energy of the molecules at a low temperature. This results in a high percentage of sucrose retention, as evidenced by experiment *d*, which shows the highest sucrose retention (1.28 percent) of the experiments studied. On the other hand, if the adsorbent is washed with water at an activated condition (75° C.), a sizable amount of sucrose molecules will be able to diffuse out of the pore and will be washed away. This results in a low percentage of sucrose retention, as illustrated by experiment *b* with 0.63 percent retention. Similar arguments apply to experiments *a* and *c*.

For the discussion of mechanisms which follows, it is to be recalled that, while the surface equilibrium adsorption decreases with rise in temperature, the pore filling sorption increases with increasing temperature due to the activated entry effect. Since the retention of sucrose is a sorption process, the mechaniism contributing to the sucrose retention should follow the same reasoning. Six possible pairs of comparison can be obtained from four sets of data. Analysis of each pair of data gives some insight into the mechanism of sucrose retention by the adsorbent.

(1) Experiment *a* and *b*: Theoretically, if the surface adsorption mechanism predominates in the system, the sucrose retention in experiment *a* should be higher than that of experiment *b*. The fact that the sucrose retention of experiment *b* is higher than that of experiment *a* suggests that the pore filling mechanism dominates the process.

(2) Experiment *a* and *c*: Both mechanisms can account for the observed experimental data, i.e., the sucrose retention of experiment *a* is higher than that of experiment *c*, as theoretically predicted by both surface adsorption and pore filling mechanism.

(3) Experiment *a* and *d*: The pore filling theory suggests, contrary to the surface adsorption theory, that the sucrose retention of experiment *d* should be higher than that of experiment *a*, in agreement with the experimental data. This is evidence against the surface adsorption model.

(4) Experiment *b* and *d*: Both surface adsorption and pore filling mechanism can explain the observed experimental results: the sucrose retention of experiment *d* is higher than that of experiment *b*.

(5) Experiment *b* and *c*: The experimental data again favor the pore filling model. The sucrose retention of experiment *b* is shown experimentally to be higher than that of experiment *c*. The result supports the pore filling mechanism theory.

(6) Experiment *c* and *d*: Conparison of experiment *b* and *c* with *a* and *d* suggests that, in the case of surface adsorption, the minimum sucrose retention for experiment *c* should be 0.63 percent and that the maximum sucrose retention for experiment *d* should be 0.45 percent. However, experimental values of 0.21 and 1.28 percent, respectively, were obtained, indicating that the theory of surface adsorption mechanism may not be applicable in the system studied. The data can best be interpreted by the pore filling theory. Table 3 summarizes the above discussion.

The foregoing argument tends to emphasize that sucrose retention is a "pore filling" mechanism. However, although the author has not yet obtained positive evidence to support the surface adsorption mechanism, it is undoubtedly true that part of the sucrose retention is attributable to the surface adsorption process. The practical application of the "activated entry" effect on the sucrose retention is obvious.

The deactivation mechanism of adsorbents as studied by "activated entry" effect. — It is well known that the color and ash removal powers of adsorbents gradually decrease with increasing length of service in the adsorption process. Many techniques can be used to investigate the mechanism of the deterioration in activity due to physical changes in the adsorbents' characteristics. An understanding of the mechanism is an obvious prerequisite in considering a rational approach for the adjustment of operation variables to reduce the rate of adsorbent deterioration. Considerable effort has been made in this respect. Evidence has been accumulated to elucidate the factors that contribute to the deactivation of the adsorbents studied: (a) Pore blockage by sorbed inorganic salts; (b) covering of carbon surface by sorbed inorganic salts; (c) occlusion of pore space and diminution of small pores by growth of hydroxyapatite crystallites; (d) filling of pores by inorganic salts and nonactive carbon; (e) pore blockage by nonactive carbon, and (f) replacement of original carbon by carbon residue of pyrolyzed organic matter. The discussion of these factors is not in the scope of this paper. In the following section, evidence is presented to show the pore blockage by sorbed inorganic salts as studied by the "activated entry" effect.

Table 3. — Mechanism of sucrose retention as elucidated by the experimental data and theoretical consideration

Comparison between experiments	Surface adsorption theory	Pore filling theory	Experimental observation	Predominant mechanism
a and b	a > b	—	b > a	Pore filling
a and c	a > c	a > c	a > c	Surface adsorption and pore filling
a and d	a > d	d > a	d > a	Pore filling
b and d	d > b	d > b	d > b	Surface adsorption and pore filling
b and c	c > b	b > c	b > c	Pore filling
c and d	c > 0.63 d < 0.45	—	c = 0.2 d = 1.28	Pore filling

Two types of pore blockage can be considered, depending on the degree of blockage. Firstly, a pore may be more or less completely blocked. Secondly, a pore may be partly blocked resulting in the formation of the ink bottle type pore. Evidence for the formation of ink bottle pores due to the service cycle can be seen from table 1, where the percentage of activated entry increases considerably for two of the adsorbents studied suggesting the possible blockage of the pore entrances by inorganic salts. To further confirm this view, two service adsorbents were treated with 0.2N hydrochloric acid in an effort to remove the sorbed ash or original ash which form constrictions at pore entrances. The results are shown in table 4.

Examination of the data obtained for service adsorbent A indicates that, for the 0.2N HCl treated sample, the amount of CTAB sorption increases and the percentage of activated entry decreases. This is most likely due to the dissolution of ash which forms the constriction at the pore entrance. The negative value of the percent activated entry is not surprising, since in the absence of the ink bottle type pores, the equilibrium adsorption should decrease with a rise in temperature. Since the hydroxyapatite is also soluble in acid, it is conceivable that part of the decrease in percent activated entry, from 14.1 percent for sample "as is" to -12.6 percent for acid treated sample, is attributable to the dissolution of hydroxyapatite at the ink bottle "neck."

Table 4. — CTAB sorption of chemically treated service adsorbents

	Sample "as is"			Sample treated with 0.2 HCl			Sample treated with 0.1 NH_4Cl		
	CTAB sorption µmoles/g. adsorbent		Percent Activated entry	CTAB sorption µmoles/g. adsorbent		Percent Activated entry	CTAB sorption µmoles/g. adsorbent		Percent Activated entry
Sample	32°C.	75°C.		32°C.	75°C.		32°C.	75°C.	
Service adsorbent A	62.3	72.5	14.1	89.8	78.5	-12.6	70.2	66	-5.9
Service adsorbent C	44.9	79.6	43.6	61.1	98.5	37.9	—	—	—

The argument is supported by the data obtained for the sample treated with 0.1N ammonium chloride which is known to dissolve calcium sulfate and calcium carbonate and leave the hydroxyapatite intact. Table 4 shows that the percent of activated entry of the 0.1N NH_4Cl treated sample decreases to a value of -5.9 percent; this implies the removal of sorbed ash at the pore entrance. Further analysis of the data reveal that the degree of decrease in percent of activated entry for the 0.1N NH_4Cl treated sample is considerably less than that for the 0.2N HCl treated sample (from 14.1 to -5.9 percent vs. -12.6 percent). The data suggests that part of the ink bottle "neck" in the adsorbent consists of hydroxyapatite. In fact, this observation may account, in part, for the presence of the ink bottle type pore in the new adsorbent. It is noted that the acid treated sample C still possesses a considerable amount of ink bottle type pore as indicated by the high percentage of activated entry (37.9 percent). Comparison of the percent of activated entry of acid treated service adsorbent A with that of acid treated service adsorbent C (-12.6 vs. 37.9 percent) suggests some basic characteristic differences in the two adsorbents. Since the acid did not remove the ink bottle pores of service adsorbent C to any great extent, it is speculated that some of the ink bottle "necks" of the service adsorbent C is formed by acid insoluble material such as carbon dioxide or silicon dioxide.

SUMMARY

Evidence indicating the presence of the ink bottle type pore in the adsorbents is supported by several independent techniques. The ink bottle type pores are found to have a profound effect on the retention of sucrose on the adsorbents due to the "activated entry" effect. The mechanism of sucrose retention is speculated to be, to a large extent, a "pore filling" process. The pore blockage of adsorbents by inorganic salts, as elucidated by the "activated entry" effect study, is given as an example, showing one of the many possible applications of the theory.

ACKNOWLEDGMENTS

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DISCUSSION

H. WALLENSTEIN: Do you think it ever will be possible to tailor-make a carbonaceous adsorbent that would selectively adsorb impurities and exclude sucrose?

C. C. CHOU: This, to some extent, depends on the mechanism of sorption - whether it is a pore-filling process or a surface adsorption process. There are several types of selectivity. For example, if the sorption is a surface adsorption process, the selectivity would depend both on the nature of adsorbates and the nature of the carbon surface; if the sorption is due to pore filling, it would depend on the molecular size of the adsorbate and on the constriction of the ink bottle pore. You would have to take mechanisms into consideration.

B. G. LOUROS: If you increased the washing temperature of the char to something above 75° C., would you drastically reduce the sucrose retention?

C. C. CHOU: According to our data, it should further reduce the sucrose retention. Unfortunately, we do not have any quantitative data in this report. The sucrose retention should decrease, since if you activate sucrose molecules inside the pore by raising the temperature, the number of sucrose molecules which are able to diffuse out should increase.

B. G. LOUROS: Do you think all of the sucrose would come out, or would some of it still be retained?

C. C. CHOU: If you use hot fresh water, and wash the chars long enough, the sucrose may eventually come out, assuming that the sucrose retention is purely a pore-filling process.

S. B. SMITH: In your work with service adsorbents, have you found that the adsorption of color or other materials has cut down the retention of sucrose? In other words, is there a displacement phenomenon involved?

C. C. CHOU: We have not done any work on this. However, it is conceivable that, in a pore-filling process, if the molecular size of the colorants is much larger than that of the sucrose, the effect of sorption of colorants on sucrose retention would be relatively small. But if the molecular size of the colorants and sucrose were comparable, there would be competition for the available pore spaces and we would expect less sucrose retention. You also would have to know the percentage of sucrose retention by surface adsorption, since in this process, the colorants would compete with sucrose for adsorption sites regardless of the relative size of these molecules.

R. N. POLLET: Were experiments shown here carried out with service char, and if so, how did the sucrose retention differ from that found when using new char?

C. C. CHOU: Yes, the experiments were done on service char. Here again, the retention of sucrose depends on the mechanism of sorption. If the surface adsorption predominates in sucrose retention, then the new char would adsorb more sucrose because of its high surface area. If the pore-filling mechanism prevails, the sucrose retention would depend on the population of ink bottle pores in each adsorbent.

F. M. WILLIAMS: Do you have any evidence to show that the radioactive sucrose is retained to a greater degree than the nonradioactive sucrose?

C. C. CHOU: Theoretically, the isotope effect for this experiment may be relatively small, since the mass ratio of carbon 14 to carbon 12 is only about 1.1. If you have a hydrogen (H_2) and deuterium (D_2) system, since the change in the mass of the atoms is large, the isotope effect could be great. This could cause a difference between the adsorption of H_2 and D_2. In our present system, we assumed that there is no isotope effect.

F. G. CARPENTER: Could you give us a little history of chars A, B, and C. A and C seem to be the same, and B seems to be quite different. What was the nature of these chars—do you have any ideas as to what made them different in their activated entry.

C. C. CHOU: The chars are from different refineries, and they are not necessarily all bone chars.

V. R. DEITZ: The model that you propose is one of many that overemphasize the geometrical structure of the carbon adsorbent. The tacit assumption is that the surface of the carbon is inert. Actually, a charcoal swells a little bit, then, upon drying, collapses. There is an alternative explanation for everything you say in terms of a more mobile carbon network which becomes hydrated, which may expand and then contract, which may be wetted in different ways, and which may have a positive temperature coefficient as you mentioned.

C. C. CHOU: I agree that there are other possible explanations for a positive temperature coefficient, but I doubt that such an explanation could account for our experimental data. For example, I find it most difficult to explain a 43.6 percent activated entry for service char C based on your argument.

REFINERY TESTING OF AN IMPROVED GRANULAR CARBON

by

S.B. Smith, H.F. Laughlin, C.G. Formeck,
Westvaco Corp.
Covington, Va.
and
Calvin O. Walters
Southdown Lands, Inc.
New Orleans, La.
(Presented by S.B. Smith)

ABSTRACT

A newly developed granular activated carbon (Suchar 681) with "builtin" pH control has been tested on a plant scale on sucrose liquors for more than five cycles of use and thermal regeneration. A parallel test with an identical plant column containing the refinery process carbon (to which deadburned magnesite had been added) demonstrated for the improved carbon a greater throughput at a given pressure drop and significantly lower volume losses on regeneration while achieving equal or better color removal. The makeup carbon contained an alkaline additive, which kept the pH control component essentially constant at an average makeup of 3 percent per cycle. Thermal regeneration conditions in the rotary kiln were carefully monitored and the structure of the absorbent critically evaluated after each regeneration. Loss of sucrose by inversion was found not to be strictly a function of pH, but for both carbons studied was affected considerably by operating variables and particularly by weekend shutdown procedures. The data show that this newly developed carbon sustained lower regeneration losses and gave improved utility over other available carbons.

INTRODUCTION

Granular activated carbon from bituminous coal was introduced to the cane sugar refining industry as a more economical alternative to bone char in the early fifties.

Extremely high decolorizing capacities were obtained, as compared to bone char, and thermal regeneration of the carbon proved satisfactory in maintaining high decolorizing activity with low regeneration losses. However, one shortcoming of such high activity refining agents, which is still little understood, is a tendency of the pH of the sugar liquors to drop appreciably as they pass through the carbon columns. Lowered pH, in turn, increases the rate of inversion in the liquor, thus leading to sucrose losses. The addition of alkaline materials in granular form to the activated carbon is one approach which has proved effective. The additive in such cases dissolves at a very slow rate and thus neutralizes the acidity produced in the column. A very dense sintered form of magnesium oxide, "deadburned magnesite," has been used effectively, but sometimes because of its high density it causes trouble by segregating within the bed, thus forming lumps which can lead to channeling in the filters and clogging of lines.

Another approach to pH control is the incorporation of the same deadburned magnesite in ground form directly into the carbon granule during its manufacture. While segregation may be reduced by this approach, the addition of the large amounts of MgO in this form required to achieve sufficient solubility can be deleterious to the carbon from a hardness standpoint.

Our objective then, in producing a new granular activated carbon, was to achieve pH control by incorporating an agent capable of holding the pH of the liquors passing through it at 7.0±0.3 units so as to minimize inversion, but which would not appreciably soften the carbon or impair its decolorizing power. Of course, this all must be accomplished without adding a significant amount of dissolved salts to the sugar.

The procedure in developing prototype materials was to test various alkaline substances as additives to carbon columns and to prepare test carbons in the laboratory incorporating the more promising substances. For screening these preparations, a laboratory column test was developed which closely paralleled plant scale performance in respect to both pH control and color removal.

Plant runs of the better formulations were then made and confirmatory column tests conducted in the laboratory. These carbons were also thermally regenerated in small quantities and retested for several cycles. A carbon was finally produced which appeared to have the desired combination of pH control, decolorizing capacity, and abrasion resistance.

However, it was recognized that full-scale refinery testing would still be necessary before the carbon could be offered with full confidence to the cane sugar refining industry.

These objectives were to a large degree accomplished, as will be shown by the data to be presented. The newly developed granular carbon designated as Suchar 681 is a bituminous coal based carbon with a size range of 12 x 40 mesh U.S. sieve series.

For the full scale refinery testing, Westvaco was most fortunate in enlisting the cooperation of Southdown Lands, Inc. At their Houma, La., refinery, a comparison could be made with their process adsorbent, Pittsburgh Cane CAL carbon, which has been in use for several years. A unique and helpful feature of this refinery is the rotary kiln which regenerates the contents of each filter separately and returns the carbon in slurry form to the same filter. The feed hopper and kiln are run empty between regenerations so that no intermixing of carbon occurs, and a good running account of the charge volume may be kept if one always refills the filter to the same level.

PLANT OPERATING EQUIPMENT

Since an excellent description of the carbon filters and regenerating kiln has been given in a previous paper[1], only a brief description will be given here.

The carbon filters are eight in number and have the dimensions shown in figure 1 taken from this publication[1], i.e., 9 feet in diameter and a 24 foot depth of carbon which is supported on a Neva-Clog screen adequately supported in a truncated cone bottom. The flow of liquors is in the downward direction and there is an outlet pipe and manhole placed above the screen in the cone bottom to permit the pumping out of the carbon in slurry form to the drain tank and regenerating kiln and to permit final manual cleanup.

The spent carbon discharged from the filter is pumped by centrifugal pumps over a dewatering screen before dropping into the open feed hopper. A small amount of fines is separated with the water draining from the screen at this point. The feed hopper has a full cone bottom with a flat screen about 2 feet above the apex to permit drainage. About a foot above the screen, a screw feeder traverses the tank and extends out into an open trough conducting the wet carbon to the feed chute of the kiln.

The regenerating kiln is a Bartlett-Snow direct fired kiln with countercurrent flow of the gases with respect to the carbon flow. The kiln is brick lined and equipped with small lifters. It rotates at a rate of about 3 r.p.m. and is fired by a long flame North American burner equipped with gas/air ratio controls to keep the gas/air mixture essentially constant throughout the firing rate range. A reasonably tight seal is maintained on the hot discharge end of the kiln by means of an asbestos sleeve bearing against the rotating shell. This sleeve is flushed with steam and additional steam is directed into the kiln with the combustion gases. The red hot carbon leaves the kiln by dropping directly into a totally enclosed quench tank filled with water and equipped with a constant level device. The mixture of quenched carbon and water is withdrawn continually from the cone bottom of the quench tank by a centrifugal pump and the carbon fed through a pipe and hose back into the filter from which it came. In general, no screening is done as the carbon returns to the filter. The transport water is drained from the bottom of the filter as it accumulates.

The water vapor and combustion gases leave the kiln at the feed end and are pulled by slight suction into a stack operating on natural draft. A tight seal is not maintained on the feed end of the kiln and some gases escape through the feed pipe. There is undoubtedly some air inleakage at this end, but probably little of it actually contacts the hot carbon.

The kiln controls consist of a temperature indicator-controller measuring the exit gas temperature. There is also an indicating thermocouple extending into the hot end of the kiln, but this is strictly a high temperature limit control which will cut off the gas when the temperature reaches the set point. The flow of gas is controlled by the exit gas temperature controller and, for a given feed setting, the hot end of the kiln reaches an equilibrium temperature which is relatively constant. The control of the hot end temperature is maintained by the trial and error setting of the gas exit temperature until the desired hot end temperature is reached. Process steam is manually controlled with a valve and flow meter and maintained essentially constant throughout a given run. Although the temperature control system may seem awkward, it works out well in practice since the firing rate is automatically adjusted in case of any sudden change in moisture level of the feed. In following the operation of the kiln during regeneration, Orsat gas analyses were made on samplings from two locations: the first where a probe could be inserted through the firewall at the firing end to sample kiln gases between the burner and

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[1] Wilson, T.A., Truemper, J. T., and Fayard, J.A. 1962. Plant scale evaluation of granular Darco. Proc. 7th Tech. Sess. Bone Char pp. 85-108

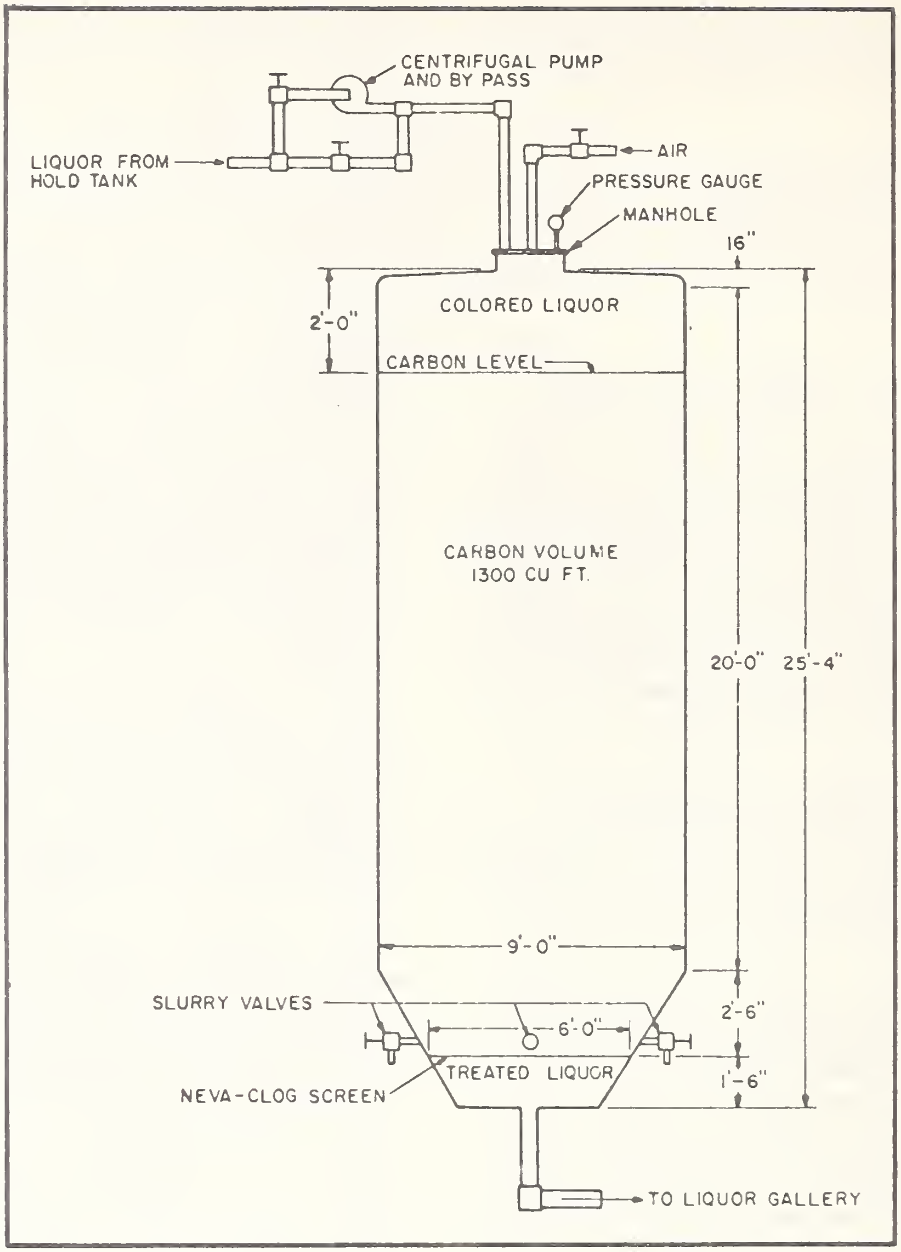

Figure 1. — Typical carbon filter design at Southdown Refinery (Wilson,[1]).

the carbon bed, and the second at the cold end of the kiln where gases were drawn from the entrance to the stack through a draft gauge tap.

FILTER OPERATION

The eight carbon filters are run downflow on lime-phosphate-clarified liquor following pressure filtration. Only six carbon filters are on stream at any one time, with each filter staying on stream between 21 to 24 days. Carbon from each filter is regenerated in the kiln in 72 to 85 hours, and the remaining off-stream time is spent in sweetening off, transferring the charge to the kiln feeder, and after regeneration, in blow down and the sweetening-on operation. A slight unbalance in the cycle timing can be taken up by running the kiln on refinery shutdown days to catch up. In conducting this experiment, it was decided to follow plant practice insofar as possible, but where warranted, to recommend changes and special trials which might bring about improved efficiency and better utilization of the carbon and regeneration equipment. In order to assist in this, two large flow meters were installed at the liquor gallery on filters

Nos. 4 and 5. Filter No. 4 contained the process carbon, Pittsburgh Cane CAL, which had been circulating in the system for a number of years. The performance of this carbon was followed as a control throughout the experiment.

The completely new charge of Suchar 681 was placed in Filter No. 5, and this necessitated the withdrawal of the process carbon by regenerating it and then bagging it off for future reuse as make-up for the other process carbon columns.

For the first filling, No. 5 column was filled about one-third with water and the dry carbon dumped from bags directly into the column until the carbon level reached the water surface, at which time more water and carbon were added as required to bring the level to within 20 inches of the neck of the filter. For the first two cycles, the Suchar 681 carbon was sweetened on downflow without removing the water surrounding the particles. This practice did not appear to yield any particular benefits and so we reverted to the standard technique of blowing down the filter to remove as much water as possible and then sweetening on in the downflow direction, after which the filter is placed on stream downflow with the liquors directed to the evaporators at the gallery. Pinpoint sized bubbles were observed in the first runnings of all the columns and gradually disappeared after a day or so on stream. At the liquor gallery, depending upon the availability of the sugar melt, both filters were adjusted to run at about 35 gallons per minute. However, lower flows were observed at times as pressure drop built up in a given column and the full flow could not be maintained even with a fully opened valve. This was particularly true of the process carbon which had to be backwashed occasionally in order to reduce the pressure drop across it. Unfortunately, it was not possible to install a volumetric totalizing meter on the two filters, but frequent readings were made on the flow meters and an average of these values used to calculate throughput on each filter.

SAMPLING AND TESTING PROGRAM

Automatic samplers were used on the feed liquor and effluents from Nos. 4 and 5 filters to collect four hour composites of each stream. On the first cycle, these samples were analyzed separately and then the data averaged to give daily figures for tabulation. However, it was soon learned that there was little variation hour to hour so that composites were made from the four hour samples, and one sample analyzed for each shift. During the early cycles, the analyses were made by Westvaco personnel, but later on the samples were composited on a daily basis and the analyses made by the Southdown personnel.

Care was taken that samples not be allowed to stand more than a few hours before putting them under refrigeration until the analyses could be made.

All liquor samples were analyzed for color by both the spectrophotometer and the Horne visual comparator. Other analyses were done by Southdown standard methods for invert content, brix by refractometer, ash by conductivity and pH by the glass electrode with temperature compensation.

FIVE CYCLE PERFORMANCE OF SUCHAR 681

It was recognized at the outset that the initial complete fill of fresh carbon would present a unique situation as compared with general refinery practice. Since the alkaline additive was expected from laboratory tests to have a somewhat higher solubility as compared to the situation following thermal regeneration, it was decided to employ a low concentration of additive in the initial fill as compared with the carbon to be used as makeup in subsequent cycles. Therefore, the magnesium compound additive was nominally 1 percent in this fill and analyzed at 0.76 percent as MgO. Since carbon handled in this system normally undergoes some water washing in the slurry handling system prior to sweetening-on, this first fill was loaded into water and given several hours water washing to remove surface alkalinity before admitting sugar liquors. When the liquors finally came up to full concentration following sweetening-on, the pH was about 8.2. Color removal and pH and inversion data are shown in figures 2 and 3 and tables 1 and 2. In spite of the high pH, the colors were excellent, indicating that the decolorizing capacity of the carbon was not appreciably affected by the high pH. By the second day on stream, the average effluent pH was 7.8, and after another twelve hours was down to 7.2. From that point on, the pH control was very good, giving an average effluent pH of 6.9 compared with an influent of 7.15.

The comparative data for the process carbon were obtained over the same period, except for the one or two days at the beginning and end of the cycle, due to the staggered operating periods of the two filters. Though the same liquor was being fed to both filters, the average color of the influent liquor to the respective columns was slightly different in certain cycles due to the different operating periods. The performance data on the first and fourth cycles are shown in figure 2. The color of the effluent on the first day was essentially zero, and the color gradually built up over six days, at which point it leveled off and continued at nearly the same level until the 24th day. Three interruptions occurred during the run: one

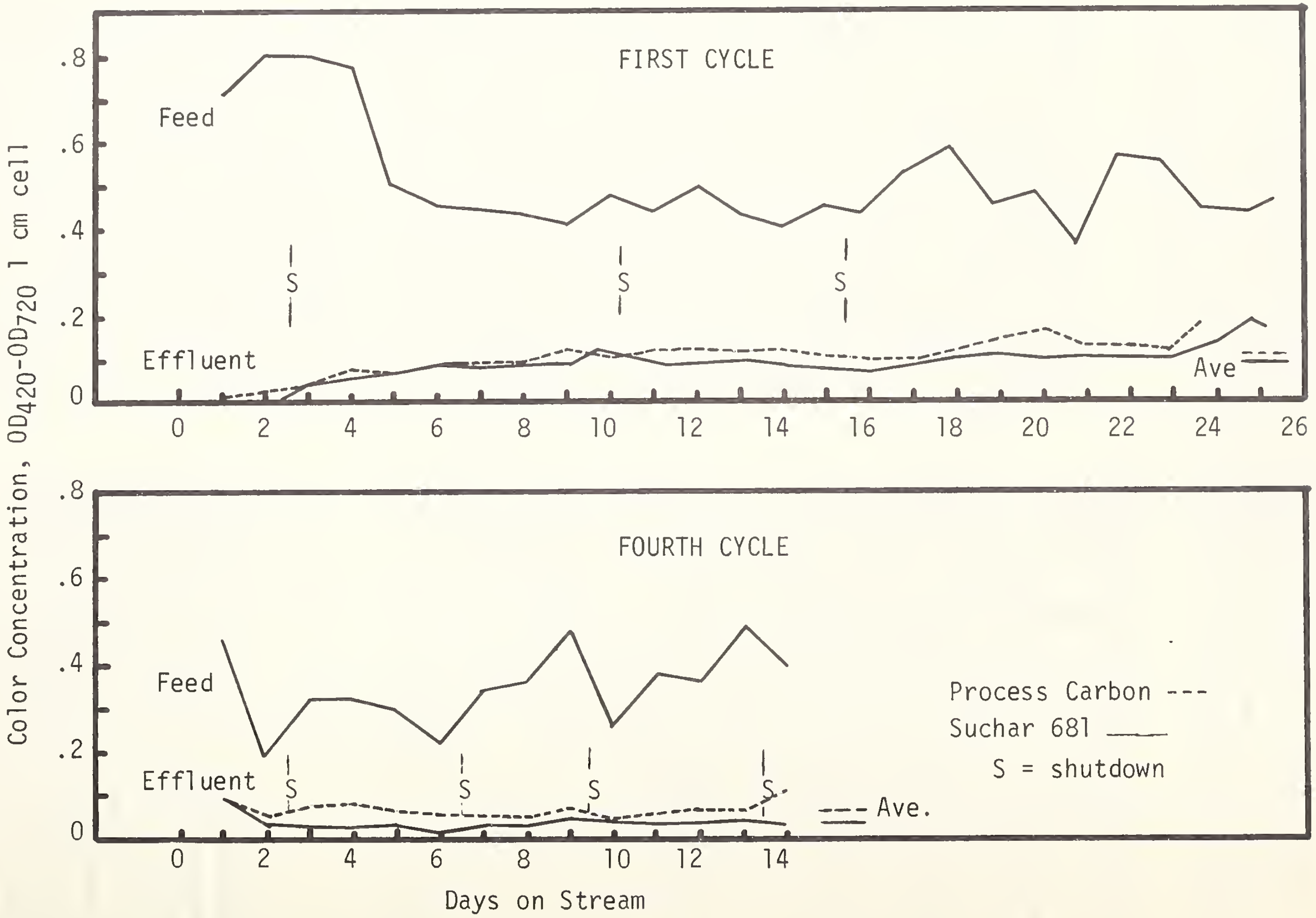

Figure 2. — Single column color removal performance for Suchar 681 and process carbon on two typical cycles.

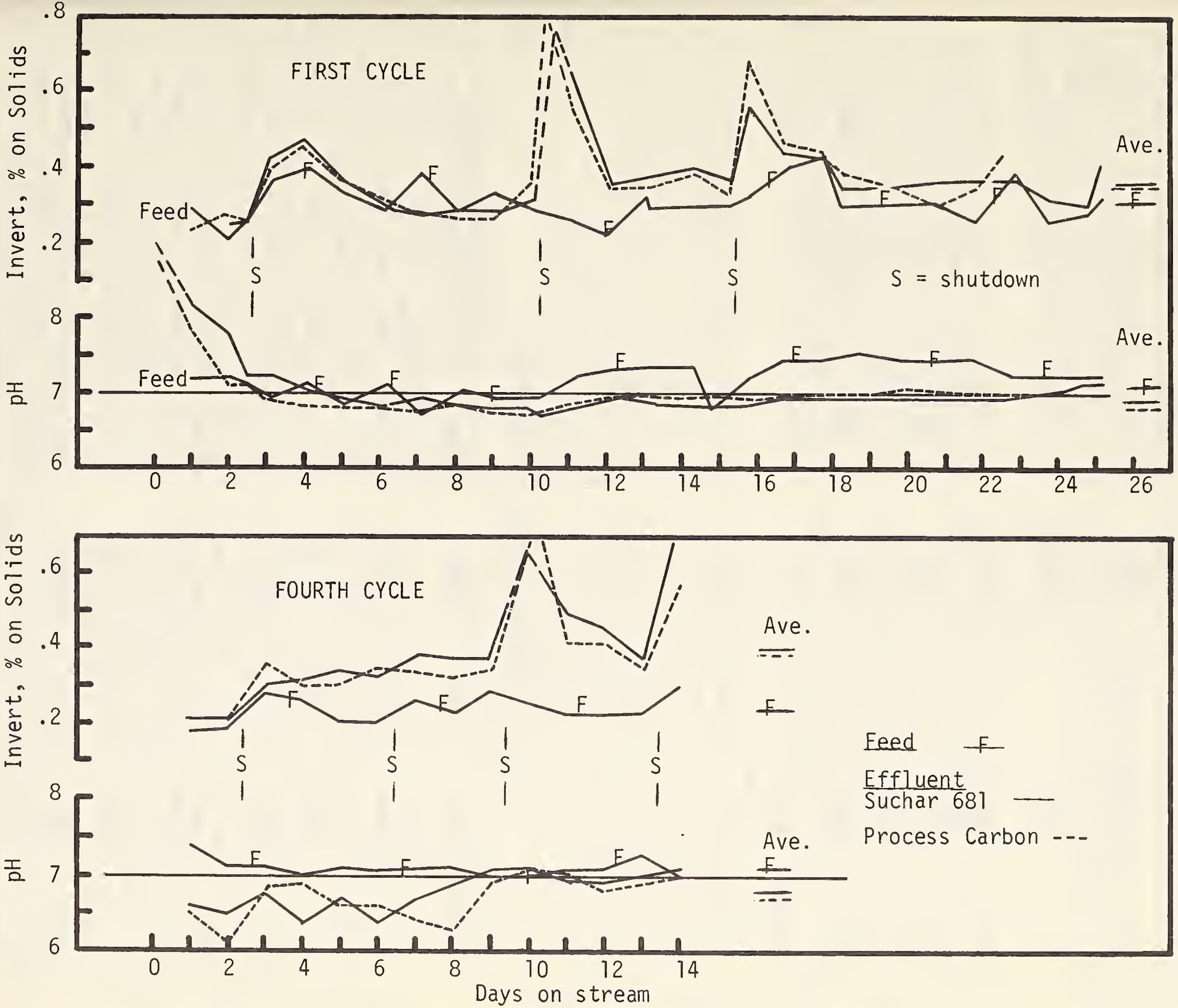

Figure 3. — Typical changes in pH and invert content in single column runs on "Suchar 681" and process carbon.

Table 1. — Comparative decolorizing efficiency of carbons

Cycle	Carbon	420 Color,OD 720		Color removed	
		Feed	Effluent	OD Units	Percent
1st	Suchar 681 — Virgin	.500	.093	.407	81.4
	Process	.504	.107	.397	78.8
2nd	Suchar	.413	.113	.300	72.6
	Process	.450	.113	.337	74.9
3rd	Suchar	.413	.081	.332	80.4
	Process	.430	.071	.359	83.5
4th	Suchar	.351	.042	.309	88.0
	Process	.351	.072	.279	79.5
5th	Suchar	.625	.069	.556	89.0
	Process	.625	.074	.551	88.2
Average	Suchar				82.6
	Process				81.0

Table 2. — Liquor pH and invert changes

		pH			Invert Percent Dry Solids		
Cycle	Carbon	Feed	Effluent	Change	Feed	Effluent*	Change
1st	Suchar	7.15	6.90	-.25	.303	.351	+.048
	Process	7.10	6.90	-.20	.301	.348	+.047
2nd	Suchar	7.00	6.90	-.10	.213	.260	+.047
	Process	7.00	7.00	0	.225	.258	+.033
3rd	Suchar	7.10	6.60	-.50	.214	.359	+.145
	Process	7.10	6.60	-.50	.216	.307	+.091
4th	Suchar	7.10	6.80	-.30	.240	.396	+.156
	Process	7.10	6.70	-.40	.240	.381	+.141
5th	Suchar	7.50	6.60	-.90	.231	.319	+.088
	Process	7.50	6.70	-.80	.231	.313	+.082
Average	Suchar	7.17	6.76	-.41	.240	.337	+.097
	Process	7.16	6.78	-.38	.242	.321	+.079

*Values on the first day of start-up following refinery shutdowns omitted from average

6 day shutdown due to high salt content in the process water, and two weekend shutdowns later in the cycle. The shutdowns had practically no effect on the effluent color or the pH, but had a drastic effect on the invert content which was very high on both filters immediately following the shutdown, as shown in figure 3. On several occasions in subsequent cycles, the sugar liquor was recirculated through the filters during the shutdown. This prevented the high invert content observed immediately after startup. Unfortunately, this technique was costly and impractical over long shutdown periods. The color removal data for all five cycles are shown in table 1.

Although the first cycle may be somewhat atypical because a full charge of fresh carbon was employed, nevertheless, the behavior is not substantially different from that of later cycles, as may be seen by comparing with the data of the fourth cycle also shown in figure 3. Excellent pH control was obtained in the first cycle with the lowest recorded pH being 6.7. The initial pH was somewhat higher because of the free alkalinity in the fresh carbon, but this did not persist longer than 2 1/2 days.

In the fourth cycle, the pH started off around 8 and dropped to 7 early in the second day. The pH dropped rather low initially, even though the feed liquor held a pH slightly over 7. However, after the ninth day, the pH began to rise, and thereafter did not fall below 6.8. Four shutdowns took place in this fourth cycle, and high inversion was noted upon startup after each shutdown. To our knowledge, recycling of the liquor was not practiced during this cycle.

In table 2, the pH and invert content of incoming and effluent liquors are shown for both the Suchar and process carbon columns for the first five cycles of use. During this period, the usual makeup of Cane CAL carbon was made on the process carbon, depending on the amount of loss in each regeneration. On the Suchar 681 column, makeup additions were made with a carbon containing slightly more additive than the initial fill, that is about 2 percent additive measured as percent MgO. In several cases the losses were less than 4 percent, but since additions had been anticipated on this basis, at least 4 percent makeup was added and the excess carbon, if any, was estimated and permitted to leave the system to the next filter. The data on pH are self-explanatory: pH drop for the first four cycles was 0.5 or less pH units for both the Suchar and process carbons. In the fifth cycle, a somewhat greater drop was observed, but this was at a point where a higher influent pH of 7.5 was used. The higher pH did not seem to be effective in preventing pH lowering, since the product pH from both filters was almost the same as in the previous cycle. In calculating the invert sugar content of the effluents, as shown in the next to the last column, the exceptionally high values obtained on the first day following each shutdown were omitted from the average. This seems to be an atypical situation depending on refinery practices peculiar to this particular installation. Change of invert content as percent on dry solids is given in the last column. The values are somewhat erratic from cycle to cycle and, in general, the process carbon showed considerable fluctuation, going as high as 0.14 percent. The Suchar carbon column also showed high invert in this range on two cycles.

Averaging the five cycles, the Suchar and the process carbon showed a difference of only 0.03 pH units, with the Suchar lowering the pH the larger amount at 0.41 pH units. There is also a slight difference in average inversion for the five cycles, with the Suchar producing 0.018 percent more invert than the process carbon. In view of the relatively high levels of inversion in both carbons, resulting mainly from the long periods of shutdown, it is not felt that this difference is significant though obviously undesirable.

In table 3, the average conductivity ash measurements for all five cycles are shown. The differences between feed and effluent are shown for each cycle in the last column. Since some values are negative and some positive, the average is very close to zero for both carbons. We can confidently say that there is no significant change in the ash content in spite of the magnesium present. On one cycle, sulfated ashes were determined and these were in the same order of magnitude, but somewhat lower than the conductivity ash measurements.

REGENERATION AND ITS EFFECTS ON CARBON PROPERTIES

The thermal regeneration of the Suchar 681 was conducted under conditions essentially the same as have been found satisfactory for the process carbon. However, as regenerations proceeded, minor changes in operation were made in the direction thought to be favorable for both carbons. In table 4, the conditions for each regeneration are shown, along with the time required to regenerate these filters and the burning losses obtained. Close attention was not accorded the regeneration of the process carbon in every case, so these conditions are omitted from the table. However, the time required to regenerate, and losses (as taken from Southdown records) have been recorded. Though Orsat analyses were run on gases from both ends of the kiln, only those from the hot end are regarded as significant and included in the table. There was considerable variation in the temperature of different runs but the usual range is from 1600° to 1675°F. The conditions of the second and third regeneration,

Table 3. — Average conductivity ash in liquors

Cycle	Carbon	Regenerations	Ash, percent on dry solids Feed	Effluent	Difference
1st	Suchar 681	0 (Original)	0.201	0.181	-0.020
	Process	X (Unknown)*	0.210	0.194	-0.016
2nd	Suchar	1	.172	.169	-.003
	Process	X+1	.172	.166	-.006
3rd	Suchar	2	.160	.186	+.026
	Process	X+2	.168	.189	+.021
4th	Suchar	3	.115	.124	+.009
	Process	X+3	.115	.125	+.010
5th	Suchar	4	.134	.131	-.003
	Process	X+4	.134	.136	+.002
Average	Suchar				+.0018
	Process				+.0022

*Estimated average life, 20 cycles (makeup at 5 percent per cycle).

Table 4. — Thermal regeneration of Suchar 681 and process carbon

Regeneration	Avg. Temp.	Gas flow	Atmosphere, Hot end			Time to regenerate	Burning losses
Number	°F.	CFH	Percent CO_2	O_2	CO	Hr.	Percent by vol.
Suchar 1	1656	2180	8.3	0.24	4.6	72	1.0
Process						87	4.0
Suchar 2	1724	2600	7.2	0	4.0	83	1.0
Process						106	8.5
Suchar 3	1848	2460	9.0	1.8	0.4	73	6.9
Process						109	3.2
Suchar 4	1620	2750	9.5	0	2.8	71	3.9
Process						80	6.0
Suchar 5	1600	2820	9.1	0	3.4	68	2.9
Process						79	2.8
Average							
Suchar						73.4	3.1
Process						92.2	4.9

however, were purposely made more severe, with the intention of bringing the density of the regenerated carbon back closer to that of the original. In the third cycle, a very high temperature was employed, and it appeared that excess oxygen was available at this time for an unknown reason. Not only is the free oxygen recorded at 1.8 percent, but the percent of carbon monoxide is very low. It may also be noted that the gas flow required to maintain this high temperature was very low, indicating that carbon was being consumed in the process. As a result, the burning loss was 6.9 percent, which is considerably higher than the losses observed in other cycles. Though some mechanical changes were made in the feeder system for maintenance reasons from time to time, nevertheless, there was a definite difference in the time required to regenerate the two identical volumes of carbon. Suchar 681, being somewhat coarser, was apparently more free-flowing and tended to feed more quickly than the process carbon. This resulted in a tendency to underburn the Suchar carbon though it will be seen from subsequent data that the buildup of density has not been detrimental as far as the quality of sugar produced is concerned. In two regenerations following the fifth, feed rate of the Suchar has been cut back to increase the overall regeneration time.

In spite of the overburning in the third cycle, the average burning losses were only 3.1 percent and for the process carbon 1.8 percent higher. The process carbon also experienced a high loss in one cycle but the reasons for this are not evident. Even if the two high loss cycles are excluded from the average, there is still a significant advantage in favor of the Suchar carbon.

In table 5 are shown the physical properties of the original and regenerated carbons in regard to screen analysis, mean particle diameter and density.

A trend can be noticed in successive regenerations of the Suchar as the plus 12 mesh material decreases and the fraction passing 40 mesh increases. Mean particle diameter, however, has not decreased significantly and the fines have not become excessive. For the process carbon, the physical properties have nearly leveled off. The average life of this carbon is probably about 20 cycles, as inferred from an average makeup of 5 percent per cycle. The averages show a much higher "through 40" fraction and a MPD of about 0.65 mm. The density is somewhat increased over the original at 31.8 lb./cu.ft. The progressive changes on regeneration are clearly evident in figure 4.

Table 5. — Physical properties of original and regenerated carbons

Carbon	Screen Analysis (U.S.) Percent						MPD	Density
	On 12	12X16	16X20	20X30	30X40	Thru 40	mm.	Lb./Cu.Ft.
Suchar 681								
Original	3.2	38.8	35.0	17.5	5.5	0.4	1.12	28.6
1st Regen.	2.6	27.0	36.0	23.7	9.3	2.0	1.03	29.6
2nd Regen.	0.8	25.8	34.8	25.4	10.1	3.1	0.98	31.2
3rd Regen.	1.5	30.4	39.2	20.5	7.1	1.4	1.06	32.5
4th Regen.	.8	25.6	37.0	22.4	10.1	4.1	1.02	32.5
5th Regen.	.3	19.2	36.7	25.8	12.8	5.2	.93	33.7
Process Carbon								
Original	.2	32.8	46.0	16.6	3.2	1.2	1.08	29.8
X+1 Regen.	.1	2.4	13.9	31.9	36.4	15.4	.63	31.7
X+2 Regen.	.1	3.1	16.9	33.4	34.2	12.3	.65	31.8
X+3 Regen.	.1	4.3	21.0	34.5	29.8	10.3	.67	32.1
X+4 Regen.	.1	2.8	16.3	30.3	34.4	16.1	.64	31.9
X+5 Regen.	0	2.6	17.3	31.2	33.4	15.5	.66	31.7
Average Regen.	.1	3.0	17.1	32.3	33.6	13.9	.65	31.8

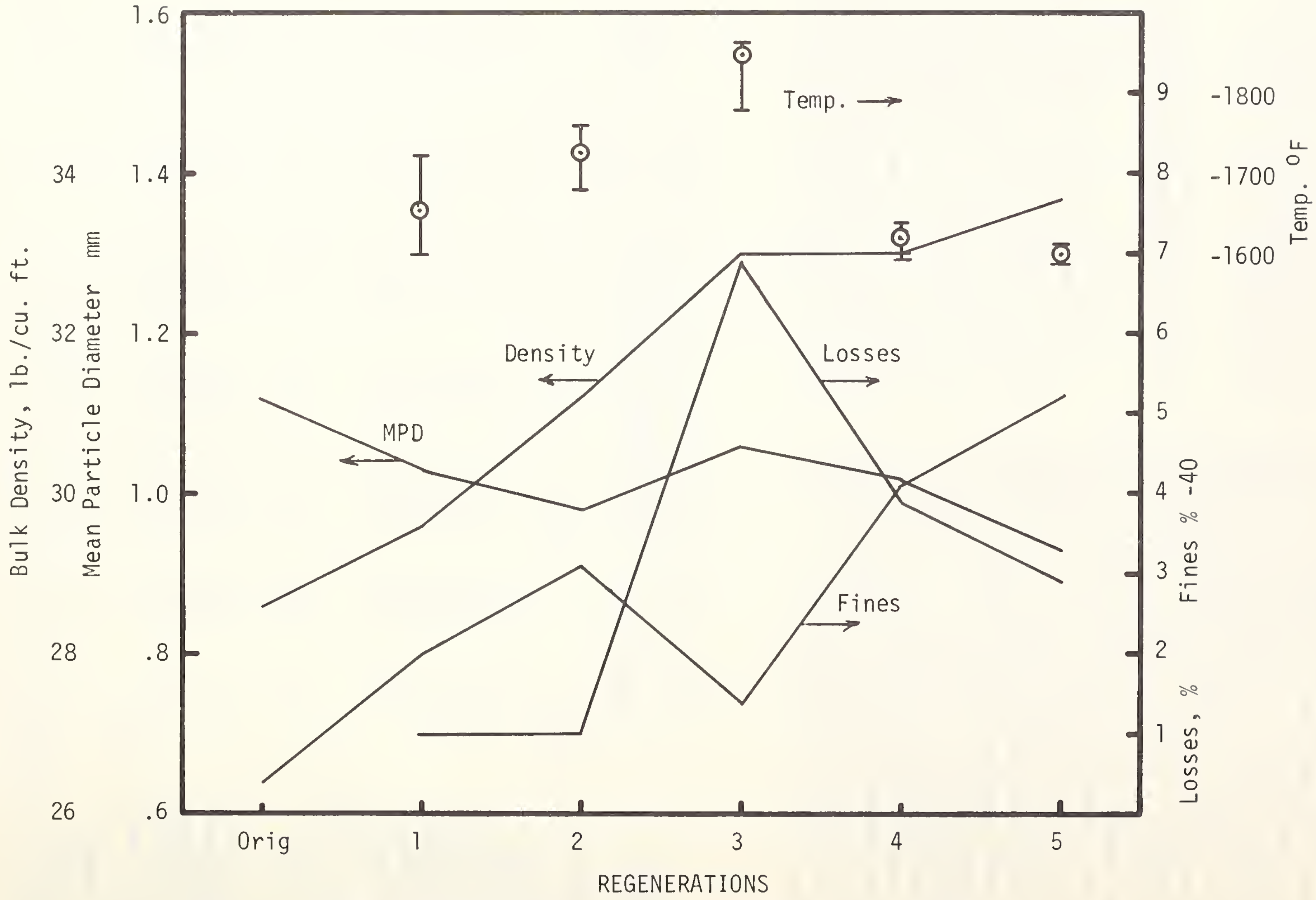

Figure 4. — Effect of temperature of regeneration on the physical properties and losses of "Suchar 681".

ABSORPTIVE PROPERTIES

In table 6 are shown the data for all regenerated and original carbons for Decolorizing Index (DI) as determined with molasses, the Iodine No., total ash, magnesium oxide content, and the bulk density in g./cc. All of these data are on a specific weight basis figured per gram of carbon except for the bulk density. Again, these properties showed definite trends for the Suchar carbon through the five regenerations, whereas the process carbon has stabilized at a steady state level. The Decolorizing Index has not changed significantly for the Suchar from its original value, as regeneration tends to increase the decolorizing power in spite of the increase in bulk density. A significant lowering of Iodine Number is observed, but part of this is due to dilution with inactive carbon, as will be seen when these data are compared on a volume basis. There is very little change in the total ash, but there is a gradual increase in the MgO content, as the makeup is added at a higher MgO level than the original carbon. Since the process carbon contains deadburned magnesite at a relatively high level, the MgO contents are significantly greater than for the Suchar. The process carbon also has a higher average level of DI indicating a better efficiency in the molasses test. Strangely enough, however, this decolorizing power is not being reflected in performance on plant liquors in spite of the finer average particle diameter of this carbon, which should have further enhanced its color adsorption rate.

These trends are perhaps better shown in figure 5, showing only the Suchar properties. The data are self-explanatory.

In order to focus attention on a constant volume of carbon such as is used in treating the liquors (i.e. a given filter contains a fixed volume of carbon regardless of the weight that may be picked up in successive regenerations), data are given on a volume basis. The values are calculated on a volume basis simply by multiplying the specific weight basis values by the apparent density in g./cc. Data so computed are shown in table 7. The trends that may be noted are somewhat different than in the preceding table. The Decolorizing Index for the Suchar has shown a pronounced increase over the original, and the drop in Iodine Number is not nearly as great in proportion to the original. The ash content appears little different from the original except for the fifth cycle. For the process carbon, the Decolorizing Index is shown to be somewhat higher than for the Suchar carbon. The ash is about the same, but the Iodine Number is appreciably lower and the MgO content appreciably higher. Trends may be better seen in figure 6. It is interesting to note the abrupt jump in the DI in the third cycle where the highly oxidizing atmosphere had its effect. We do not know why the ash increased abruptly in the last cycle, but there is an indication that the Iodine Number is leveling off, which is a good sign.

Table 6. — Properties of regenerated carbons (weight basis)

Carbon	Decol. Index DI/g.	Iodine No. mg./g.	Total Ash Percent	MgO Percent	Bulk Density g./cc.
Suchar 681					
Original	11.9	1300	8.6	.76	.458
1st Regen.	12.1	1194	7.7	.32	.475
2nd Regen.	11.8	1096	7.6	.36	.500
3rd Regen.	12.2	992	7.8	.43	.521
4th Regen.	12.3	874	7.5	.61	.521
5th Regen.	11.3	828	8.4	.88	.540
Process Carbon					
Original	10.8	1025	12.8	5.59	.478
X+1 Regen.	13.4	568	9.1	2.40	.508
X+2 Regen.	13.7	591	9.2	2.10	.510
X+3 Regen.	12.7	581	9.0	2.10	.514
X+4 Regen.	13.6	550	8.8	2.40	.511
X+5 Regen.	12.9	558	-	-	.508
Average	13.3	570	9.0	2.25	.510

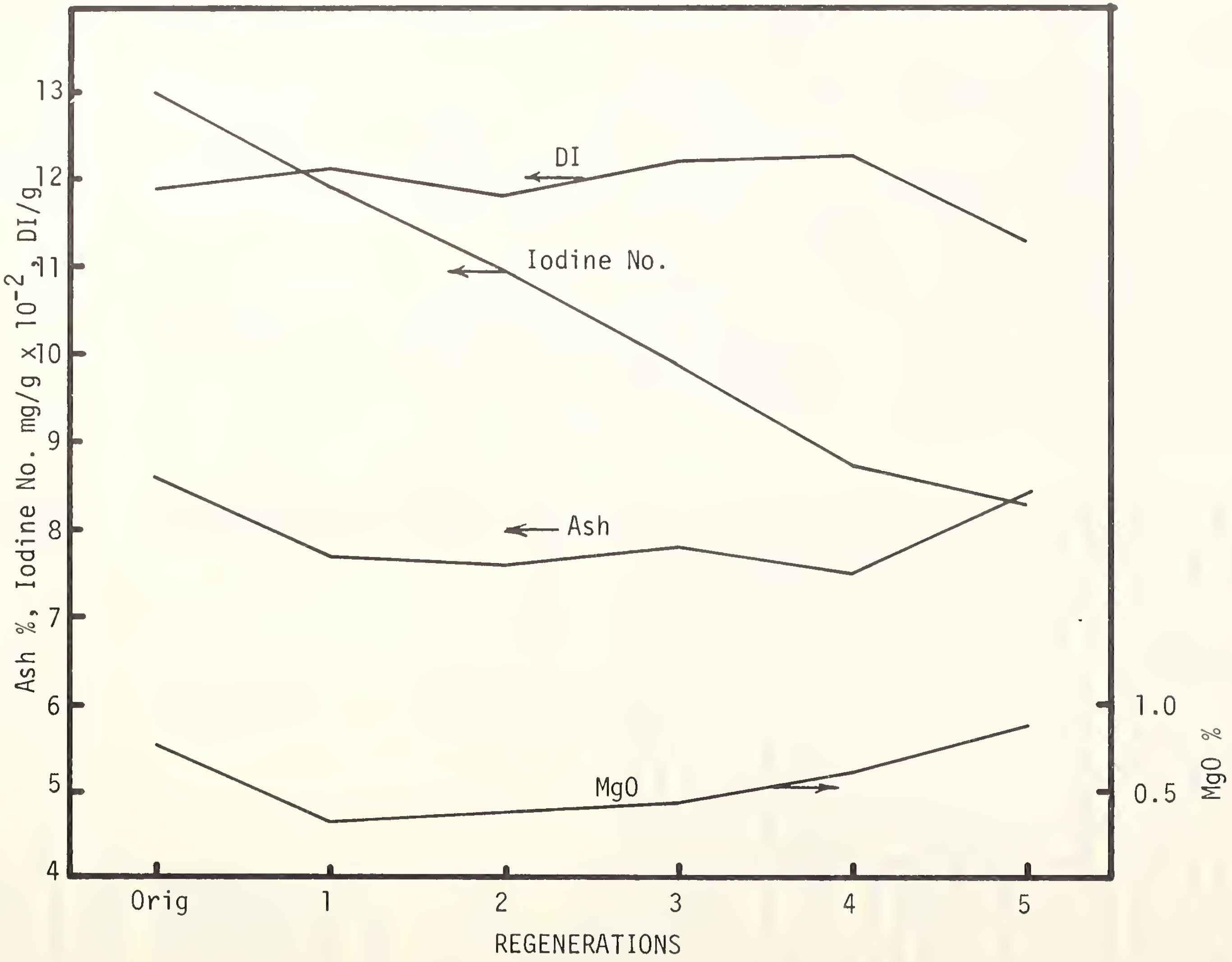

Figure 5. — Properties of the original and regenerated "Suchar 681" on a weight basis.

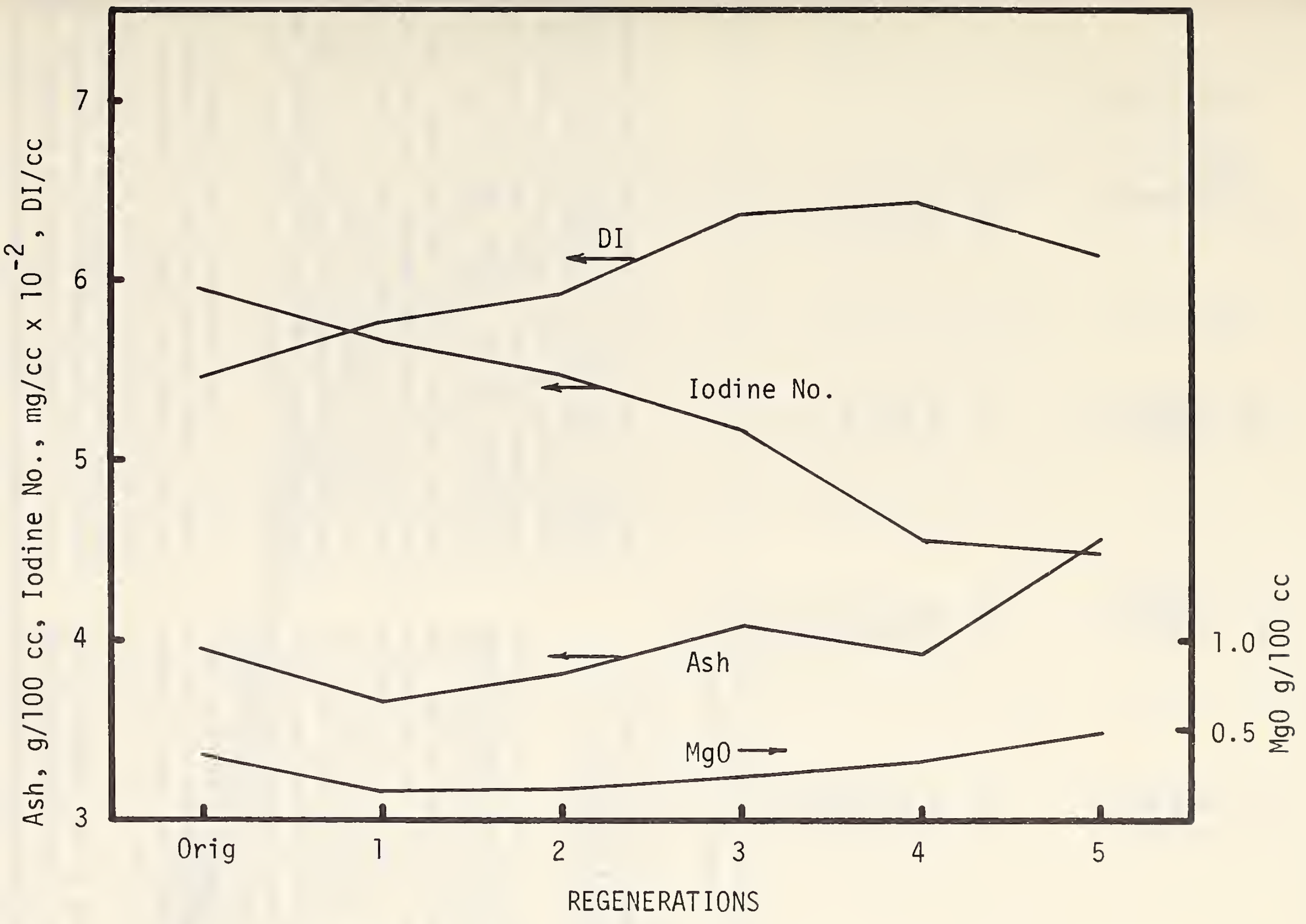

Figure 6. — Properties of the original and regenerated "Suchar 681" on a volume basis.

Table 7. — Properties of regenerated carbons (volume basis)[1]

Carbon	Decol. Index DI/cc.	Iodine No. mg./cc.	Total Ash g./100 cc.	MgO g./100 cc.
Suchar 681				
Original	5.45	595	3.94	0.35
1st Regen.	5.75	567	3.66	.15
2nd Regen.	5.90	548	3.80	.18
3rd Regen.	6.36	517	4.06	.22
4th Regen.	6.41	455	3.91	.32
5th Regen.	6.10	447	4.54	.48
Process Carbon				
Original	5.16	490	6.12	2.67
X+1 Regen.	6.81	289	4.62	1.22
X+2 Regen.	6.99	301	4.69	1.07
X+3 Regen.	6.53	299	4.63	1.08
X+4 Regen.	6.95	281	4.50	1.23
X+5 Regen.	6.55	283	-	-
Average	6.77	291	4.61	1.15

[1] Datum by Vol. = Datum/g. X Bulk Density, g./cc.

CHANGES IN MACROPORE AND MICROPORE STRUCTURE ON REGENERATION

In order to determine more precisely what might be happening to various chars as they undergo thermal regeneration, pore structure determinations were carried out using generally accepted methods. The macropores lying between 150 Å. and 10 microns were determined by a high pressure mercury porosimeter[2]. In this determination mercury is admitted to an evacuated sample of carbon, and then the degree of penetration of the mercury measured as the pressure is increased and successively smaller pores are penetrated. The pressure readings are then converted to a corresponding pore diameter, and a distribution curve calculated on the basis of a gram (or cubic centimeter) of carbon. An Aminco mercury penetrometer was used in the tests.

A distribution of pores in the micropore range running from 10 to 150 Å. was determined by the method of Juhola et al[3] using the water desorption isotherm. Using the Kelvin equation, which assumes capillary condensation of the water in the pores, the relative pressure of water vapor may be converted to a corresponding pore size and the weight of water taken up calculated over to a volume of water per cc. of carbon. For this work, the cosine for the Kelvin equation was taken as 0.49 and the molar volume of water as 20 cc. Since the procedure is tedious and time consuming, not all the samples were examined by the water adsorption technique. In figure 7 are shown the pore structure curves for Suchar 681 in the original state for the first, third, and fifth regenerations. Also included is one determination on the process carbon.

Table 8 shows incremental measurements of the volume between various pore sizes. It is revealing in that there is hardly any change in the pore volumes on regeneration in the 0 to 15 or 15 to 19 Å. range. However, in the 19 to 25 range, there is a pronounced drop in pore volume, and for the process carbon, the volume in this range is extremely low. It appears that

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[2] Frevel, L.K. and Kressley, L.J., 1963. Anal. Chem. 35: 1492-1502.

[3] Juhola, A.J., Palumbo, A.J., and Smith, S.B., 1952. Jour. Amer. Chem. Soc. 74: 61-64.

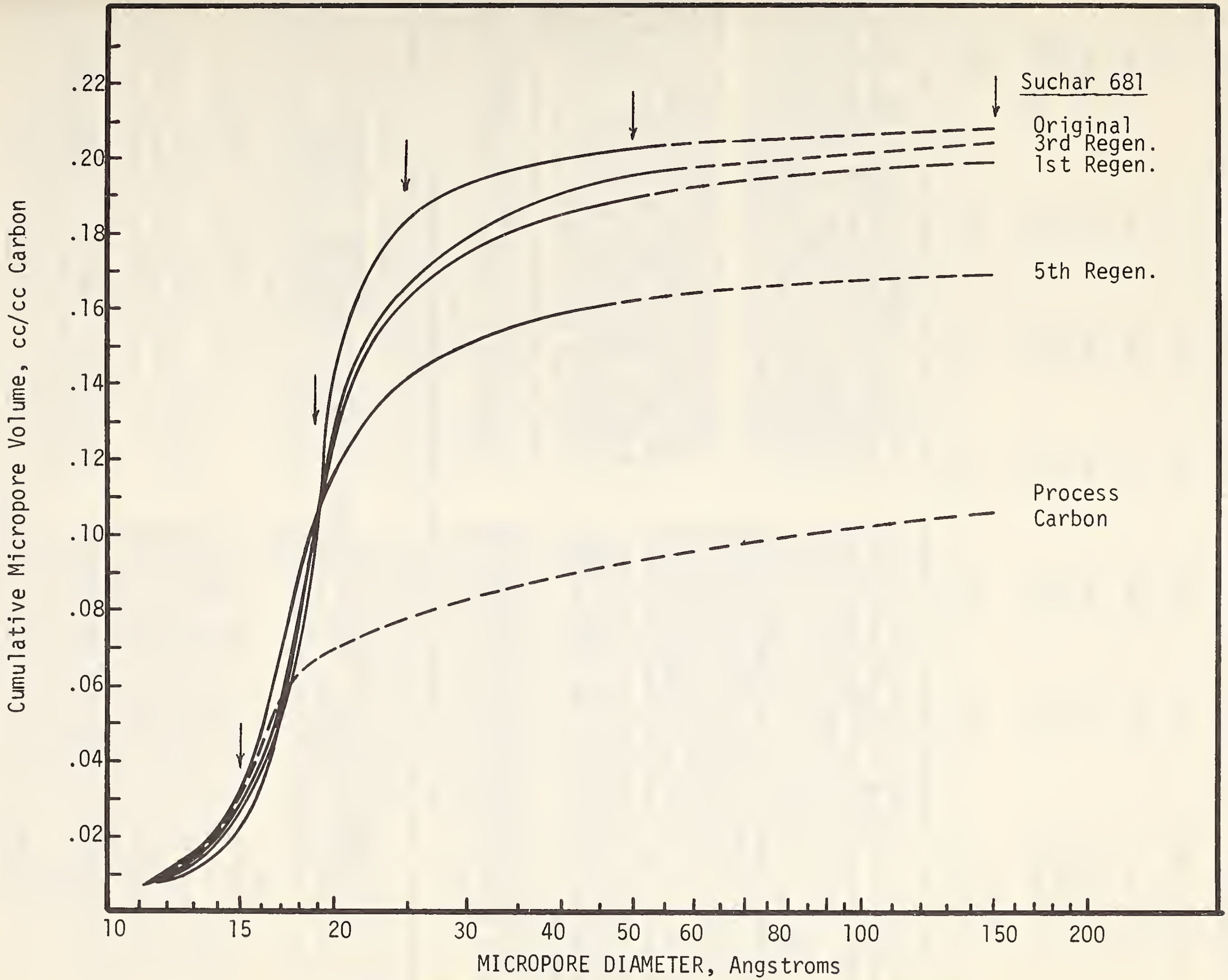

Figure 7. — Cumulative micropore volumes as a function of micropore diameter.

Table 8. — Incremental micropore volume distribution

	Volume per diam. interval, cc./100 cc. carbon					Total Micropore
Pore diam. increment	0-15	15-19	19-25	25-50	50-150 Å	0-150 Å
Carbon						
Suchar 681						
Original	2.6	8.4	7.3	1.9	0.5	20.7
1st Regen.	2.1	8.9	5.1	2.8	.9	19.8
3rd Regen.	3.1	7.9	5.4	3.1	.8	20.3
5th Regen.	3.1	7.3	3.7	2.1	.8	16.9
Process						
X+5 Regen.	2.6	4.2	1.0	1.4	1.8	10.6

in the thermal regeneration process, this particular range of pores is being lost, either by burning out to a larger size or by filling in with carbon; the latter is probably more likely. There is little change in the 25 to 50 Å. range, but these changes are more or less in keeping with the DI changes. This is the range which is probably the most active in decolorizing and purifying the sugar solutions. There is also a contribution in the 50 to 150 Å. region, but the volume here is quite small and does not contribute a large amount of surface area. The total micropore volumes shown in the last column indicate a slight downward trend for the Suchar, and a lowering to about one-half for the process carbon. The only conclusion we may draw is that what micropore volume is being lost in successive regenerations is not effective in the sugar purification operation.

In table 9, the macropore volume distributions are shown. In this case little in the way of trends can be noticed. The total macropore volume for the Suchar appears to be increased slightly at the fifth cycle, and for the process carbon a considerably higher figure is noted. It could be that some of the micropores are being enlarged to fall into the macopores region. Surprisingly, the total pore volume of the carbons, as shown in the last column, including both micropores and macropores, has not changed appreciably.

Since it is generally accepted that the internal surface of the carbon is the primary physical quantity which results in purification by adsorption, the data have been converted from "pore volumes" to "pore areas" by rough calculation, as shown in table 10. These data indicate that in the 0 to 15 Å. range there is a slight increase in surface area, and in the 15 to 19 range, a slight decrease. The process carbon, however, shows about half the surface area in this range. In the 19 to 25 region where the pore volume has been reduced, there is, of course, a corresponding decrease

Table 9. — Macropore volume distribution by Hg penetration (volume basis).

	Volume per diam. interval, cc./100 cc.				Total Macropore	Total pore vol.*
Pore diam. Å	150-1M	1M-10M	10M-30M	30M-100M,	150-100M,	0-100M Å
μ	.015-.1	.1-1	1-3	3-10	.015-10	0-10μ
Suchar						
Original	4.9	6.4	2.6	.7	14.6	35.3
1st Regen.	5.2	5.9	2.2	1.1	14.4	34.2
3rd Regen.	5.4	6.8	2.4	1.2	15.8	36.1
5th Regen.	5.7	7.7	2.4	.9	16.7	33.6
Process						
X+5 Regen.	7.0	9.3	2.6	.6	19.5	30.1

*Including micropore volume by water adsorption.

Table 10. — Calculated surface areas vs. adsorptive properties

Pore Diam. Å Calc'd. at	Calc'd. Surface Area in m.^{2}/cc. Carbon 0-15 14	15-19 17.5	19-25 22	25-150 35	SA 0-150	Iodine No. mg./cc.	Decol. Index DI/cc.
Suchar							
Original	74	192	132	27.5	426	595	5.45
1st Regen.	60	203	93	42.3	398	567	5.75
3rd Regen.	88	181	98	44.7	412	517	6.36
5th Regen.	88	167	67	33.2	355	447	6.10
Process							
X+5th Regen.	74	96	18	36.6	225	258	6.55

in surface area, and the process carbon is even lower than any of the Suchars. However, in the 25 to 150 range there appears to be a maximizing in the first and third regenerations for the Suchar and a rather high figure for the process carbon. It is interesting to note by comparing these surface areas to the Decolorizing Index that a reasonably good correlation is obtained.

If one considers the surface area in all pores from 0 to 150, which would come close to approximating the total surface area of the carbon, one should obtain a good comparison with the Iodine Number as shown in next to the last column. Here, quite a good correlation is obtained except for the first and third regenerated samples which are quite close together, but in inverted order.

One therefore sees from the pore structure analysis that an explanation can be made for the changes in Decolorizing Index and the reduction in Iodine Number as well. Up to this point there has been no reduction in performance properties of the carbon, but it is interesting to conjecture whether the Iodine Number can go appreciably lower without bringing about some unfavorable results. If that were the case, of course, it would only be necessary to increase the severity of the regeneration conditions so that Iodine Number could be restored to a higher level.

SUMMARY AND CONCLUSIONS

In table 11 are shown the comparative performance data on the Suchar 681 vs. the process carbon over the five successive cycles covered by this paper.

Resistance to flow. — Over the entire period the process liquors passed more freely through the Suchar 681; the average observed flows on the two columns are shown in the first data column. The duration of the filter runs, though not determined by any final color criterion, is given so as to permit calculation of total sugar treated as shown in the next column.

Color removal. — The total color removed is calculated in arbitrary units by multiplying the average optical density reduction for each run by the pounds of sugar treated. The makeup carbon required to maintain the original fill volume is given in the last column for each regeneration.

Over the first five adsorption cycles the Suchar 681 treated 3 million pounds (10.9 percent) more sugar than the process carbon and from this extracted 6.8 percent more color. Obviously, if the flow rate and length of run could have been increased on the Suchar column to give an equal color removal, a still greater advantage in sugar purified would have been realized and the make up requirement further reduced.

Attrition resistance. — Under the prevailing operating conditions considerably less makeup was required for the Suchar for the five cycles, amounting to a makeup of only 3.14 percent per cycle. This constitutes an advantage for the Suchar of 1.76 percent per cycle or a 36 percent smaller loss per cycle.

Using the average throughput and makeup requirements for the five cycles, the burn ratios were calculated as 0.545 and 0.623 lb. of carbon per 100 lb. of sugar, for Suchar 681 and the process carbon, respectively. The makeup ratio for an average cycle was then only 0.017 lb. carbon per 100 lb. of sugar for Suchar 681. This compares with a loss of 0.031 for the process carbon, indicating a 45 percent lower makeup ratio for the Suchar 681.

Table 11. — Summary of comparative performance

Carbon cycle	Average flow g.p.m.	On stream Days	Sugar treated Million lb.	Color removed Δ OD×lb./10^6	Makeup required percent by vol. fill
Suchar 1	33.1	25.3	8.07	3.28	1.0
Process	27.7	23.6	6.20	2.46	4.0
Suchar 2	33.1	20	6.24	1.87	1.0
Process	28.0	27.3	7.05	2.38	8.5
Suchar 3	30.0	22.3	5.96	1.98	6.9
Process	30.0	19.3	5.16	1.85	3.2
Suchar 4	35.0	14	4.50	1.39	3.9
Process	30.0	14	3.85	1.06	6.0
Suchar 5	31.0	23	6.46	3.59	2.9
Process	28.2	23	5.88	3.24	2.8
Total 5 cycles			31.22	12.11	15.7
			28.14	11.34	24.5
Suchar 681 advantage			3.08	.77	-8.8
Suchar 681 advantage percent			10.9	6.8	-1.8/Cycle

Burn ratio, lb. C/100 lb. sugar — Suchar 681 .545
Process .623

Makeup ratio, lb.C/100 lb. sugar — Suchar 681 .017
Process .031

A further comparison may be made with the data of Wilson[1]. Though conditions in the refinery may well have been different in 1960, nevertheless makeup losses for granular Darco carbon were reported to be 5.3 percent by volume, or, for the burn ratio of 0.627 lb. carbon per 100 lb. of sugar, 0.033 lb. of makeup carbon per 100 lb. of sugar. Suchar thus shows a makeup advantage of 0.016 or 48 percent. The color removal capability of the Darco column relative to the process carbon was judged to be equal at that time.

Hydraulic properties and processing flexibility. — It therefore appears that Suchar 681 satisfactorily maintains its color removal capability on successive regenerations while undergoing substantially less attrition or burning loss. This carbon is significantly harder than other granular carbons and maintains a coarser particle size distribution with a lesser fines content at equilibrium. This makes for a more free-flowing filter, thus enabling (a) the processing of higher Brix liquors at equal pressures, (b) higher flow rates at the same sugar solids level, or (c) tandem operation of filters with less pressure head loss. Thus, with some modifications of refinery practices, a typical refinery could benefit, at the refiner's option, by either greater refining output, improved final colors, or lower burn and makeup ratios.

pH Control. — The objectives in pH control and inversion control were not completely achieved, but a substantial improvement over unbuffered activated carbon was realized since in laboratory tests pH's as low as 5.0 have been obtained. It was evident that insufficient alkaline additive was employed in this initial plant test. Fears that additive contents of more than 1 percent as MgO in a completely virgin fill might cause color problems appear to have been unfounded. Thus, in subsequent production runs, higher additive contents amounting to 2 to 2-1/2 percent have been employed. This change, together with slightly more severe regeneration conditions should result in greatly improved pH and inversion control in spite of makeup in the 3 percent range.

Economics-inversion losses vs. makeup savings. — Though inversion losses certainly are not to be taken lightly, it is worth noting that savings in makeup can easily outweigh such losses. A rough calculation of such savings may be made for a 1 million lb./day refinery over a 300 day production year. If sugar loss is calculated at 7¢/lb. and makeup carbon costs at 29¢/lb., the following savings are realized for Suchar 681 as compared with the process carbon taken at the same price:

	Makeup lb./100 lb. sugar	Inversion increase Percent
Suchar 681	.017	.097
Process carbon	.031	.079
Difference	-.014	+.018

Makeup saving: 10^6 lb./day × 300 day/yr. × 1.4 × 10^{-4} lb. C/lb. × \$.29/lb.C = \$12,200/yr.

Sugar loss: 10^6 lb./day × 300 day/yr. × 1.8 × 10^{-4} × \$.07/lb. = \$3,780

Net savings \$8,420/yr.

If a longer cycle (or higher throughput) were used as suggested, further savings in gas consumption, evaporator steam, and wash water would also be realized.

Conclusions. — Though the foregoing conclusions may appear somewhat presumptuous, they have nevertheless been borne out by four additional cycles conducted since the original oral presentation of these data.

Judging from the reasonable success of this first well-documented plant test plus the experience of other users of Suchar in similar but less controlled plant tests, it is evident that a pH controlled granular activated carbon of improved decolorizing efficiency and greater attrition resistance is now available to the sugar industry.

ACKNOWLEDGEMENT

The authors wish to thank sincerely the management of Southdown Lands, Inc., for the privilege of conducting the tests in their Houma, La., plant. Particularly, we are indebted to John Campbell, Scott Waldrip, William Grillet, Robert Picou and many others who worked most conscientiously in conducting operations and gathering analytical data.

DISCUSSION

K.R. HANSON: Do you think that the Iodine No. of the regenerated carbon that was falling will reach a floor eventually, or will it keep right on down to a very small number, even smaller than the service char you measured it against? What effect is this going to have on decolorization?

S.B. SMITH: Observing over a number of cycles, we see the Iodine No. levelling off by the fifth cycle, on a volume basis. In fact, we now have completed two more cycles and the indication is that it has really reached a level. It may vary somewhat in subsequent cycles, but we expect it to level off around the 600 value on a weight basis. This apparently is not low enough to cause any problems in cane sugar decolorization. It may affect adsorption of some compounds that we are not measuring, but, to this date, we have not seen any difficulty from low Iodine Number.

F.M. CHAPMAN: I see that the mean aperture (M.A.) of your carbon was relatively large, and it appears that the cycle was not nearly long enough to exhaust the capacity of the carbon. Have you done any work on the effect of varying the contact time? With this large M.A., the specific resistance will be low, so that you could get fairly high rates of flow. Have you done any work which would tell us, for instance, the difference between 2 hours, 4 hours, and 6 hours transit time?

S.B. SMITH: In the laboratory we have run columns at various rates of flow. If we keep the same relative residence time, it matters little whether we have a deep bed and a fast flow, or a shallow bed and a slow flow. Therefore, we feel that with this coarser particle size, we certainly could filter in a tandem filtration with double the flow rate. In effect, one could keep the filter on stream longer before reaching a color break. Also, one could cut off the upstream column for regeneration, and have attained in it a higher degree of saturation than in the downstream filter, which would constitute a net gain in terms of countercurrent efficiency, and a lowering of the burn ratio.

F.M. CHAPMAN: In addition to that, there will likely be a substantial reduction in capital costs of the plant.

S.B. SMITH: Yes, probably that's right.

L. MAHONEY: Do you have any experience beyond the five cycles?

S.B. SMITH: We've now carried the experiment through 8 cycles of adsorption and regeneration. We've found that these trends have more or less continued — that is, about the same invert formation occurs. The pH control has not been quite as good, we believe, because we need to "burn" a little harder to reduce the bulk density and free up the pH additive.

We have leveled off, however, at a density of around 34.4 lb./cu.ft., which does not seem to have had a deleterious effect on the color removal, as this has remained essentially at the 80+ percent level.

P.F. MEADS: Is your carbon compatible with others? Could you have mixed your carbon with the process carbon and come out all right?

S.B. SMITH: Yes, they're very close in density, and the mean particle size being a little bit larger would not have any great effect. The carbons will simply blend together and there would be no segregation.

J.F. DOWLING: In the initial run, the pH of liquor off virgin char for the first 24 hours was up above 8. Now that you've gone through 6 or 7 cycles, is the pH below 8 for the first 24 hours?

S.B. SMITH: By the time the filter is sweetened on, you get down to around pH 8, and then it drops quite quickly in the first day down to the 7 region. So there's only a very brief period of liquor flow between 7 and 8, and this does not affect the decolorization; you still get essentially water-white liquors during this period.

G.A. HAGENEY: Were the colors that you have adjusted for pH?

S.B. SMITH: Yes, they were all adjusted to pH 7 ± 0.2.

G.A. HAGENEY: You used the 420 and 720 method. Did you use the Bottler's Formula, where you multiplied the reading at 720 by 2?

S.B. SMITH: No, we did not put it on the solids content basis, nor did we multiply by 2 or any other number. We just subtracted the reading at 720 from the 420 reading for a 10 cm. cell.

SECOND SESSION: W. R. Tuson, Colonial Sugars Co., Chairman

FILTERABILITY TESTS USING MILLIPORE FILTERS

by

John P. Sullivan
SuCrest Corporation
Brooklyn, N.Y.

ABSTRACT

A method of expressing filterability of sugar liquors which is not time dependent has been devised. More leeway is allowed with experimental conditions of measurement than with the standard test. Comparisons of the filterabilities of related laboratory and process liquors demonstrate the utility of the test.

PRINCIPLES OF FILTRATION OF SUGAR LIQUORS THROUGH MILLIPORE FILTERS

Correlation of Millipore filtration data and process data was reported by Coll and others (2) at the 1963 meeting of Sugar Industry Technologists. In collaboration with Southdown, Inc., Coll filtered 15 Brix solutions of raw sugars, clarified juices, and evaporated syrups though 1.2-micron filters for 20 minutes at 20 inches vacuum and ambient temperature. Apparently, 15 Brix solutions were used to correspond with the Brix of clarified juices from Southdown's Greenwood factory. Further results, which included data for affinated sugars at 15 Brix, were summarized by Coll in 1964 (1). Coll reported a correlation between filtration data for raw sugars and evaporated syrups.

In 1966, Pearson and Amento (6) reported a correlation between Millipore filtrations of affinated sugars at 15 Brix and solids through the filter presses of American Sugar Company's refinery in Chalmette, La. Amento's procedure was to filter through 1.2-micron filters for 10 minutes at 22 inches vacuum and 25° C.

Most of the filterability methods in industry literature, including those mentioned above, use the volume collected during a specified time interval as an indication of filterability. This volume is then compared with that of a standard sugar if the filterability is to be expressed as a ratio or percentage. In any constant-pressure filtration, however, the filtration rate is constantly decreasing. Filterability values expressed as collected volumes vary with the measurement times which are specified in the method.

By contrast, it is possible to express filterability values obtained from filtrations with Millipore filters as data which are not time dependent. If a liquor is free of suspended solids, the time for each unit volume to flow through a Millipore filter at constant pressure vacuum will be constant, or:

$$T/V = b \qquad (1)$$

where T is time, V is volume, and b is a constant which depends on the experimental conditions: e.g., Brix, viscosity, temperature, pressure or vacuum, membrane porosity.

The presence of insolubles leads to an added term:

$$T/V = kT + b \qquad (2)$$

where k (ml^{-1}) is a constant which depends on the quality of the liquor being filtered. If T is expressed in seconds and V in ml., it is convenient to express the filterability constant as K, where

$$K = 10^4 k. \qquad (3)$$

The fewer the insolubles in the sugar liquor, the nearer to zero will be the value of K. Table 1 lists values of K of 60 Brix sugar liquors of varying quality filtered through 1.2-micron filters at 22 inches vacuum and 25° C. The sucrose syrup in table 1 was prepared from a quality refined sugar. The filtered liquor and clarified (unfiltered) liquor in table 1 were

Table 1. — Values of K for sugar liquors in figure 1

Liquor	$K(ml. \times 10^4)^{-1}$
Sucrose syrup	2.0
100 percent filtered liquor	13
80 percent filtered liquor/ 20 percent clarified liquor	31
60 percent filtered liquor/ 40 percent clarified liquor	64
40 percent filtered liquor/ 60 percent clarified liquor	112
100 percent clarified liquor	330

representative process liquors and were mixed in varying proportions to provide samples with a fairly broad spectrum in insolubles content. The data from which table 1 was obtained are plotted in figure 1.

It will be noted that equation 2 fits the data for all six samples and that the practical upper limit of K is about 300. Process liquors such as clarified (unfiltered) liquors approach or exceed this limit. Measurements of liquors with values of K exceeding this limit will be discussed subsequently.

K as used in this report corresponds to the notation of Hermans and Bredee (4), who evolved equations for four general types of filtration. An explanation of each type follows:

Cake Filtration. The particle size of the insolubles is much larger than the pores of the filter medium. A cake of either compressible or non-compressible particles builds on the surface of the filter.

Complete Blocking. The particle size of the insolubles is approximately equal to the pores of the filter medium. As the filtration proceeds, each filter pore is completely blocked by one particle.

Standard Blocking. The particle size of the insolubles is much smaller than the pores of the filter medium. Buildup of particles inside each pore of the filter medium causes a gradual annular restriction.

Intermediate Blocking. The particles have gelatinous characteristics and are capable of deforming their shapes. The filtration type is between cake filtration and standard blocking, but does not correspond to complete blocking.

The filtration type is thus seen as an interrelationship between the particle size of the insolubles and the pore size of the filter medium.

The two most common types of filtration are cake filtration and standard blocking, in which the particles are either larger or smaller, respectively, than the filter pores. Experimental data indicate that filtration of sugar liquors through Millipore filters follows the standard blocking equation of Hermans and Bredee, which corresponds to equation 2 of this report.

As stated previously, the value of b depends on the experimental conditions. Filtration of sucrose syrups provides the most accurate evaluation of b, since sugar liquors of lower quality may have the same Brix but differ in viscosity. For sucrose syrups filtered through 1.2-micron filters at 60 Brix, 22 inches vacuum, and 25° C., the value of b is approximately 0.91. For sucrose syrups at 50 Brix, the value of b is

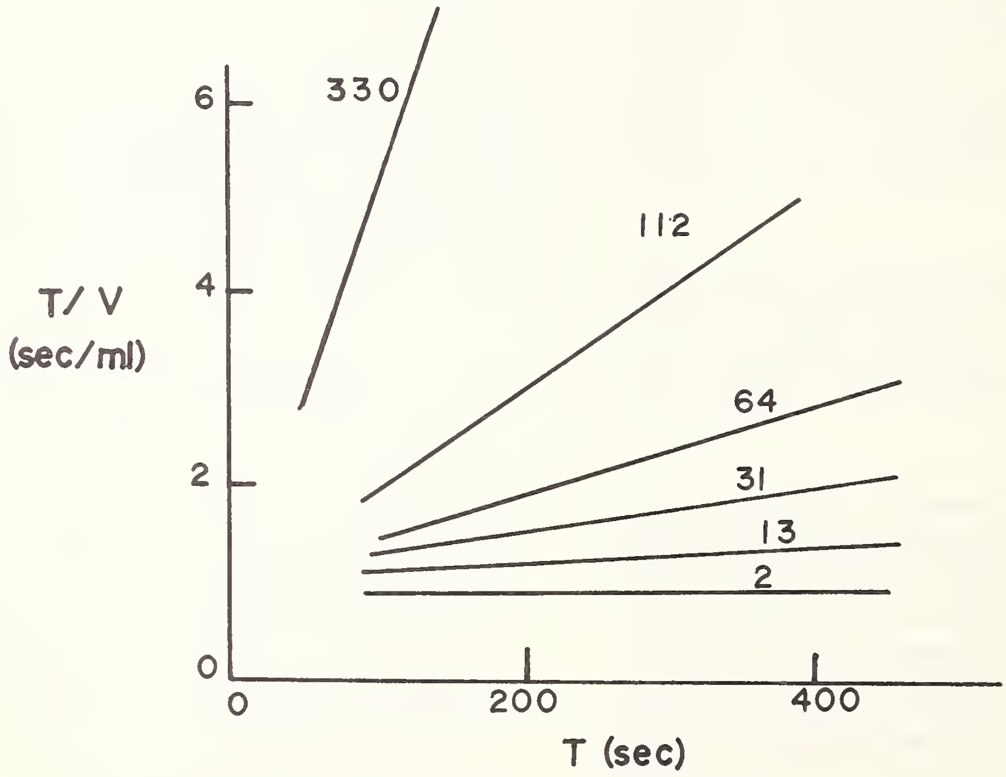

Figure 1. —Filterability plot for a wide range of sugar liquors.

approximately 0.32; at 15 Brix the value of b is approximately 0.04.

The value of b may vary with the individual filter being used. This is, however, immaterial since K can be calculated from the standard blocking equation as follows:

$$K = \left[\frac{\frac{T_2}{V_2} - \frac{T_1}{V_1}}{T_2 - T_1}\right] \times 10^4 \qquad (4)$$

One can then calculate b for the particular set of experimental conditions as follows:

$$b = \frac{T_2}{V_2} - kT_2. \qquad (5)$$

When filterability values of sugar liquors are expressed in terms of values of K, somewhat more leeway is allowed with experimental conditions because one is estimating filterability, not from the volume that flows during a certain time, but rather from the continuous increase in resistance to flow that occurs while a volume flows. A sugar liquor will have the same value of K whether filtered at 24° or 26° C., 21 or 23 inches vacuum, or through a "slow" or "fast" filter, since these experimental conditions affect flow rate but not the relationship between filtrate volume and filter resistance. Changes in experimental conditions change the value of b but not the value of K. Experimental conditions should, of course, be closely specified; however, these parameters affect fluidity more than filterability.

Equations which can be evolved from the standard blocking equation and which can be useful in evaluating Millipore filtration data are as follows:

Rate of flow (R), defined as dV/dT

From (2): $V = \frac{T}{kT + b}$

$$R = \frac{dV}{dT} = \frac{b}{(kT + b)^2} \;. \qquad (6)$$

Since $(kT + b)^2 = \left(\frac{T}{V}\right)^2$

$$R = \frac{dV}{dT} = \frac{bV^2}{T^2} \;. \qquad (7)$$

Change in rate of flow, dR/dT

From (6) and (2):

$$\frac{dR}{dT} = \frac{-2bkV^3}{T^3} \;. \qquad (8)$$

Change in cumulative flow rate

From (2): $\frac{V}{T} = \frac{1}{kT + b}$

Therefore: $\Delta\left(\frac{V}{T}\right) = \frac{1}{k(T + \Delta T) + b} - \frac{1}{kT + b} =$

$$\frac{-k\Delta T}{\left(\frac{T}{V} + k\Delta T\right)\left(\frac{T}{V}\right)} \;. \qquad (9)$$

Equation 9 enables us to predict, for example, the decrease in cumulative flow rate between 4 and 10 minutes of filtration from a knowledge of k and T/V after 4 minutes.

The data in table 2, typical of Millipore filtrations, are presented to illustrate the use of some of the equations derived thus far. A plot of T/V against T is presented in figure 2 to show that the standard blocking equation is applicable.

Table 2. — Filtration of Clarified liquor from Brazilian raw sugar, affinated and clarified in laboratory through 1.2-micron Millipore filter, 60 Brix, 25° C.

Time (Sec.)	Volume (ml.)	T/V
120	56	2.14
240	85	2.82
360	104	3.46
480	115	4.17
600	123	4.88

Evaluation of K

From (4): $K = \left(\frac{3.46 - 2.14}{360 - 120}\right) \times 10^4$

$$= 55\ (\text{ml} \times 10^4)^{-1}.$$

(The use of 2-minute and 6-minute data to calculate K is arbitrary. One can always use least-squares equations if greater precision is required. It is probable that a certain amount of bleeding of insolubles occurs during the first minute or so of filtration, depending on the quality of the liquor. It is suggested, therefore, that the 2-minute data be the first ones used in calculating K.)

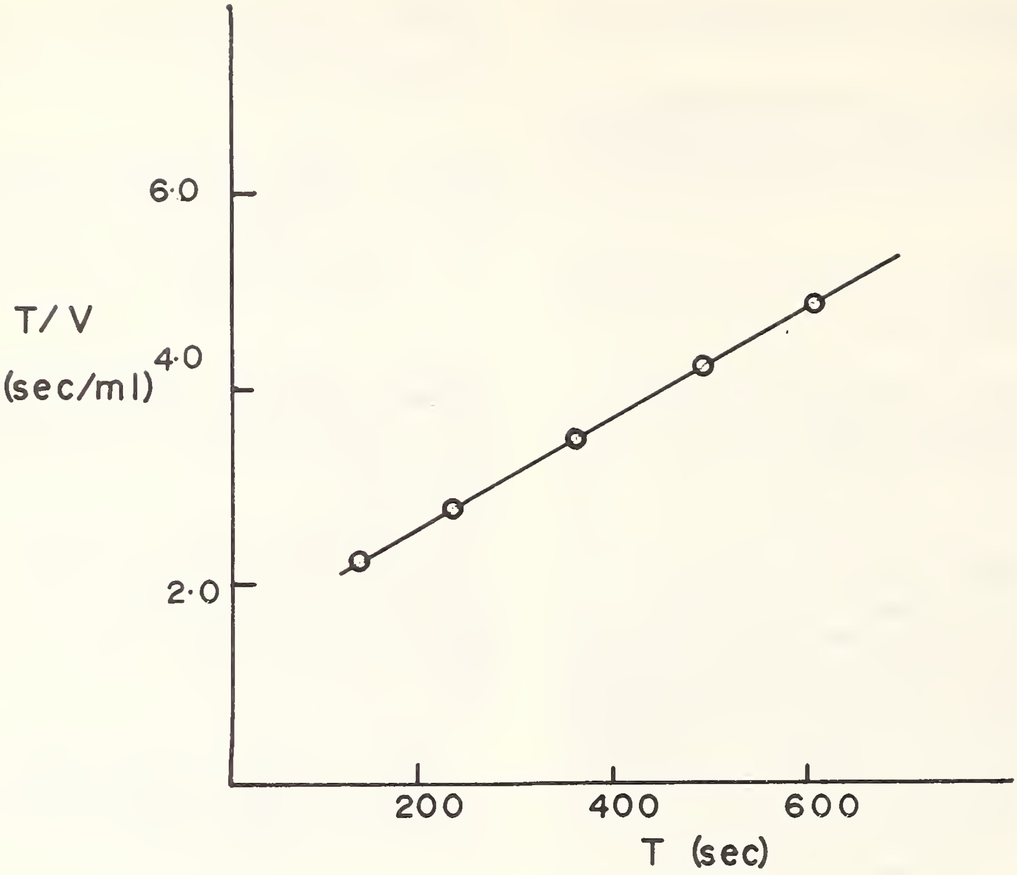

Figure 2. — Typical filterability plot.

Evaluation of b

From (5): $b = 3.46 - (55 \times 10^{-4})(360)$

$= 1.46$ sec./ml.

Rate of flow at T = 240 sec.

From (7): $R = \frac{(1.46)(85)^2}{(240)^2}$

$= 0.19$ ml./sec.

(This contrasts with the cumulative rate of flow at T = 240 sec., which is 85 ml./240 sec. or 0.35 ml./sec.)

Change in rate of flow at T = 240 seconds

From (8): $\frac{dR}{dT} = -\frac{2(1.46)(55 \times 10^{-4})(85)^3}{(240)^3}$

$= -7.3 \times 10^{-4}$ ml./sec.^{2}

Change in cumulative flow rate from T = 120 seconds to T = 360 seconds

$k\triangle T = (55 \times 10^{-4})(360 - 120) = 1.32$

From (9): $\triangle\left(\frac{V}{T}\right) = -\frac{1.32}{(2.14 + 1.32)(2.14)}$

$= -\ 0.18$ ml/sec.

SELECTION OF EXPERIMENTAL CONDITIONS

Although equation 2 can be applied over a wide range of experimental conditions, the following were thought to have the greatest applicability for filtration tests involving sugar liquors:

Brix. It was decided to filter at 60 Brix since this is the approximate Brix of many process liquors. Further dilution was avoided because of unfamiliarity with the solubility characteristics of filtration-impeding substances.

Temperature. Filtrations were at 25°C. for more precise control of the viscosity of the filtering liquor.

Vacuum. Sucrose syrup at 60 Brix was filtered through 1.2-micron filters at various inches of vacuum. It was found that cumulative filtration rates, briefly summarized in table 3, increase with applied vacuum up to 22 inches. It was decided to filter at 22 inches vacuum, the minimum vacuum for maximum flow rate.

Table 3. — Filtration of sucrose syrups vs. applied vacuum, 1.2-micron Millipore filter, 25° C.

Inches of vacuum	Cumulative rate (grams/second) After 4 min.	Cumulative rate (grams/second) After 8 min.
16	0.82	0.79
18	.98	.94
20	1.17	1.13
22	1.34	1.28
24	1.33	1.29
26	1.29	1.25
28	1.31	1.27

Filter porosity. The liquors described in table 1 were filtered through filters of the following porosities: 5 micron, 3 micron, 1.2 micron, 0.8 micron, and 0.45 micron (table 4). The 5-micron filter responded variably with increasing insolubles; the 0.45- and 0.8-micron filters were found to have too small a pore size for filtrations over the entire range. Both the 3-micron and the 1.2-micron filters responded predictably with increasing insolubles. (It was found that filtration rates were faster with the 1.2-micron filter over the entire range of liquors.) The 1.2-micron filter (RAWP047SI) was chosen for use over the 3-micron filter because of supposed greater emphasis on the uniformity of this size filter by Millipore Corporation.

Table 4. — Filtration of sugar liquors vs. filter pore size, 22 inches vacuum, 25° C.

Liquor	Cumulative rate (grams per second) after 4 min.				
	5μ	3μ	1.2μ	0.8μ	0.45μ
Sucrose syrup	1.84	0.96	1.31	0.76	0.20
100% F	1.70	.85	1.05	.55	--
80%F/20%C	.72	.60	.79	.45	--
60%F/40%C	.50	.40	.53	.24	--
40%F/60%C	.59	.31	.36	.12	--
100%C	.16	--	.15	--	--

F: Process-filtered liquor.
C: Process-clarified liquor.

In this study, filters were prewetted before vacuum was applied, so as to be able to apply 22 inches of vacuum at zero time. An occasional filter did not appear to prewet properly: that is, a white area appeared on the filter. These filters were not used. Otherwise, no particular selection was made of filters.

APPLICATIONS

Evaluation of refined sugars. — Several investigators, among them Hibbert and Phillipson (5), have used membrane filters to measure quantitatively the amount of extraneous, water-insoluble matter in refined white sugars. Some of these procedures require pretreatment of the filter to obtain a constant tare weight. Others specify the use of a matched pair of filters, e.g., AAWPO470M, supplied by Millipore Corporation.

It is suggested here that information concerning subvisual particles can also be inferred from filtration data (table 5). Some liquid sugars have values of K less than 1.0, indicating that they are remarkably free of insolubles. The values of K for syrups prepared from refined white sugars typically vary from about 2.0 to 20. Repeated filtrations do not appear to lower the value beyond that obtained after the first filtration.

Table 5. — Values of K for sugar syrups

Time (Sec.)	Volume of sugar syrups (ml.) Liquid sugar	Refined sugar syrup First filtration	Refined sugar syrup Second filtration	Refined sugar syrup Third filtration
120	128	98	107	110
180	191	138	155	160
240	250	172	202	208
300	308	202	249	255
K	2	15	5	5

This raises the question as to which comes first, the standard sugar or the standard filter. A suggested answer is that, in methods in which it is desired to use a standard sugar to calibrate filters, a sugar with a very low value of K be used.

Evaluation of process liquors.

(1) Introduction — Some of the more obvious problems in correlating laboratory and process data are: large variations may exist in individual cargoes of raw sugar; the refiner may be processing a mixture of cargoes rather than an individual cargo; raw sugar affinated in the laboratory may differ substantially from raw sugar affinated in the refinery; sweetwaters and remelt sugars may be recycled into the melt stream; laboratory clarifications, under comparatively

static conditions, are more efficient in separating muds from liquors than refinery clarifications; laboratory filterability tests are usually constant pressure (or vacuum) tests while refineries filter at constant rates or on demand; filter aid requirements vary with different raw sugars while most laboratory tests using filter aids use a standard amount of a standard filter aid; laboratory filtration data is obtained from short-cycle filter media while process filtration data is obtained from long-cycle filter media.

Succeeding paragraphs illustrate how Millipore filters were used to study the filterabilities of three raw sugars in SuCrest's Brooklyn refinery, which uses lime-phosphate clarification followed by press filtration. During this study insight was gained towards solution of many of the aforementioned classic objections to laboratory filterability tests. The emphasis on this study was on measuring, not solids throughout, but rather the quality of the liquor at each process station.

(2) Laboratory affination and clarification procedures — The laboratory affination procedure used in this study is that of the American Sugar Company[1]. The clarification procedure used in this study is presented as Appendix A. It was found that sufficient information could be obtained by clarifying at 0.025% P_2O_5 at 7.0 pH and at 7.5 pH each, in duplicate. These two pH's were sufficiently apart to have distinguishable and measurable effects on mud formation. The typical laboratory clarified liquor was of high quality, often requiring the use of a strong light for discernment of insolubles. But the Millipore filter was very effective in distinguishing among duplicate clarifications, so that a third determination was required in about one case in eight. (Values of K for laboratory clarified liquors obtained from raw sugars of various national origin are presented in Appendix B of this report. This data and succeeding data are not presented as being necessarily representative of the specified national origin.)

(3) Philippine Raw Sugar (July, 1969). This raw sugar had great cargo variations in polarization, ash, color, invert, etc. It was speculated that the darker portions of the cargo, in particular, would adversely affect filterability.

(3a) Analysis of the raw and affinated sugars. — Approximately one-fourth of a cargo of Philippine raw sugar received in July, 1969 was medium in color. The rest of the cargo was a very dark raw sugar. Table 6 is an analysis of the cargo extremes.

Table 6. — Analysis of cargo extremes of Philippine raw sugar

Sugars	Lighter portion	Darker portion
Raw sugar		
Moisture (vac-4hr. at 70° C.) percent	0.27	0.65
Invert (L & E) percent	.92	1.81
Direct polarization at 20° C.	+97.80	+95.88
Ash (sulph) percent	.268	.480
Affinated sugar:		
Ash (sulph) percent	.071	.121
Color (ICUMSA-1958, Method 2)	167	347

(3b) Laboratory treated and clarified liquors. — The laboratory affinated sugar from each portion of the cargo was laboratory clarified with 0.025% P_2O_5 and adjusted to 7.0 pH with lime saccharate as in Appendix A. The resulting clarified liquors were filtered through Millipore filters with results shown in Table 7:

Table 7. — Values of K for cargo extremes of Philippine raw sugar

Sugars	K
Clarified liquor from lighter portion of cargo	18
Clarified liquor from darker portion of cargo	23

(3c) Refinery-treated liquors (aerated and separated in the laboratory). — The low values of K in Table 7 indicated that this raw sugar had comparatively very good filterability. However, the Brooklyn refinery includes into its melt stream remelt sugars and miscellaneous sweetwaters which are not used in laboratory clarification tests. Both the appearance and the low polarization value of this raw sugar indicated that substantial amounts of remelt sugars would be produced during processing.

The laboratory clarification procedure consists of addition of treatment chemicals (phosphoric acid and lime saccharate) followed by aeration in a Waring blendor, heating to 190° F., and 15 minutes settling time. During a 5 day period, eight samples of refinery treated liquor were taken after the refinery had added phosphoric acid and lime saccharate but before aeration. They were immediately introduced into the aeration step of the laboratory clarification procedure. Aeration was followed by heating to 175° F. (to correspond with the average operating temperature of the Brooklyn clarifiers) and 15 minutes settling time. Estimates of the quality of the clarified liquors obtained from these refinery treated liquors, in terms of values of K, were then obtained by Millipore filtrations. The results follow in table 8.

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[1] American Sugar Company Form 2021-65g, Exhibit C (December 1967) (Contract No. 9).

Table 8. — Values of K for refinery treated liquors aerated and separated in the laboratory

Date	Time	P_2O_5 Percent	pH	K
7/12/69	2:00 p.m.	0.031	7.2	18
7/14/69	2:30 p.m.	0.031	6.7	19
7/14/69	5:30 p.m.	0.031	6.8	14
7/15/69	9:30 p.m.	0.031	7.0	21
7/15/69	1:15 p.m.	0.031	7.1	18
7/16/69	10:30 a.m.	0.031	7.3	20
7/16/69	1:15 p.m.	0.031	7.25	24
7/17/69	10:00 a.m.	0.031	7.25	20

Table 7 shows that the values of K obtained from the cargo extremes were 18 and 23. Since the values of K obtained (Table 8) from eight samples of refinery-treated liquor aerated and separated in the laboratory ranged from 14 to 24, indications are that the introduction of remelt sugars and sweetwaters into the melt stream had no effect on the filterability of this particular raw sugar.

(3d) Refinery-clarified liquors. — Table 8 showed that the refinery treatment station was adding amounts of chemicals sufficient for effective clarification. It was decided to compare filtration data of refinery clarified liquors with the values of K in table 8. Seven samples of refinery clarified liquor were taken during 7/14/69 to 7/18/69. Data from Millipore filtrations of these clarified liquors are summarized in table 9.

Table 9. — Values of K for refinery clarified liquors

Date	Time	pH	K
7/14/69	2:15 p.m.	6.65	198
7/14/69	5:30 p.m.	6.8	116
7/15/69	9:30 a.m.	6.95	215
7/15/69	1:15 p.m.	6.6	247
7/16/69	10:30 a.m.	6.55	90
7/17/69	10:00 a.m.	6.75	292
7/18/69	2:45 p.m.	6.8	145

A comparison of tables 7, 8, and 9 indicates that, for this particular raw sugar, fluctuations in the quality of the refinery clarified liquor were more likely caused by variable clarifier efficiency than by variable quality of refinery treated liquors.

(3e) Refinery-filtered liquors. — Refinery personnel indicated that the filtration of this particular raw sugar was "very good." (Negative comments were made about other processing aspects of this raw sugar, but this report is concerned with filterability.) On 7/17/69 (10:00 a.m.), samples from each filter press were Millipore filtered. Table 10 illustrated how Millipore filtration can be used to give quantitative values to the quality of filter press effluents.

Table 10. — Values of K for refinery filtered liquors

Press No.	Time on (hr.)	Pressure (lb./in.^{2})	K
1	2.5	25	1.8
2	6	50	2.5
4	1.5	15	4.0
7[1]	10	5	5.7
8	5	40	5.4

[1] Check press.

(3f) Conclusions

(1) Comparison of data from table 7 and 8 indicated that laboratory affinations were comparable to process affinations.

(2) For this particular raw sugar, the introduction, in considerable quantity, of remelt sugars and miscellaneous sweetwaters into the melt stream had no measureable effect on filterability.

(3) For this particular raw sugar, the efficiency of the clarification system was the chief variable in the quality of the liquor entering the filter presses.

(4) Fiji raw sugar (July, 1969). This raw sugar was characterized by excellent polarization, ash, color, invert, etc. However, the muds produced in the refinery clarifiers foamed excessively.

Analyses of the raw and affinated sugars, laboratory treated and laboratory clarified liquors, refinery treated (aerated and separated in laboratory), and refinery clarified liquors are given in tables 11 to 14.

Table 11. — Analysis of Fiji raw sugar

Raw sugar		Affinated sugar	
Moisture (vac-4 hr. at 70° C.) percent	0.28	Ash (sulph) percent	0.038
Invert (L&E) percent	.57	Color (ICUMSA 1958, Method 2)	86
Direct polarization at 20° C.	+98.65		
Ash (sulph) percent	.245		

Table 12. — Values of K for laboratory treated and clarified Fiji raw sugar

P_2O_5 percent	pH	K
0.025	7.0	30
.025	7.5	16

Table 13. — Values of K for refinery treated liquors aerated and separated in the laboratory

Date	Time	P_2O_5 percent	pH	K
7/29/69	9:45 a.m.	0.025	6.9	10
7/29/69	1:30 p.m.	.025	7.15	19
7/30/69	10:30 a.m.	.025	6.7	20
7/31/69	6:00 p.m.	.022	6.75	26
8/1/69	9:30 a.m.	.025	7.05	45
8/1/69	1:15 p.m.	.022	7.1	44

Table 14. — Values of K for refinery clarified liquors

Date	Time	pH	K
7/29/69	9:45 a.m.	6.7	80
7/29/69	1:30 p.m.	6.7	39
7/30/69	10:30 a.m.	6.55	55
7/31/69	6:00 p.m.	6.45	72
8/1/69	9:30 a.m.	6.8	160
8/1/69	1:15 p.m.	6.6	101

(4a) Comments. — From 7/29 to 7/31 the refinery-clarified liquor was of good quality in terms of filterability; on 8/1 the quality decreased. The following probably contributed to the decrease in quality:

(1) Clarifier throughout increased on 8/1; before this, start-up difficulties in other processing areas made the refinery treatment and clarification stations operate more slowly up to 8/1.

(2) The muds produced by this sugar during clarification foamed more than usual. During the night of 7/31 to 8/1, the P_2O_5 content was decreased from .025 percent to .022 percent to reduce the amount of foaming muds being formed. The lowered P_2O_5 content eventually led to a decrease in the quality of the clarified liquor (as measured visually by process personnel), so during the midnight-8 a.m. shift the P_2O_5 content was increased to .028 percent. The morning shift returned the P_2O_5 content to 0.025 percent.

The changes in P_2O_5 content, while dictated by necessity, probably contributed to the decrease in quality of the clarified liquor as measured by the value of K obtained at 9:30 a.m. on 8/1. By 1:15 p.m. on 8/1, the quality of the clarified liquor had improved; however, the P_2O_5 content at treatment station had again been decreased to .022 percent because of foaming muds. The effects of these cyclical P_2O_5 adjustment could not be followed further because shortly afterwards the refinery began processing another raw sugar. (This has been presented in detail to show how data from Millipore filtration correlated with adjustments in process treatment chemicals.)

(5) Brazil raw sugar (August, 1969). — Millipore filtration data were useful in selecting a process clarification pH. Analyses of the raw and affinated sugars, laboratory treated and clarified liquors, refinery treated liquors (aerated and separated in the laboratory), and refinery clarified liquors are given in tables 15 to 18.

Table 15. — Analysis of Brazil raw sugar

Raw sugar		Affinated sugar	
Moisture (vac-4 hr. at 70° C.) percent	0.59	Ash (sulph) percent	0.120
Invert (L & E) percent	.72	Color (ICUMSA-1958, Method 2)	308
Direct polarization at 20° C.	+97.13		
Ash (sulph) percent	.665		

Table 16. — Values of K for laboratory treated and clarified Brazil raw sugar

P_2O_5	pH	K
0.025	7.0	50
.025	7.5	73

Table 17. — Values of K for refinery treated liquors aerated and separated in the laboratory

Date	Time	P_2O_5 percent	pH	K
8/4/69	3:00 p.m.	0.030	7.15	40
8/5/69	9:30 a.m.	.028	7.55	105
8/5/69	11:30 a.m.	.028	6.7	40
8/5/69	1:30 p.m.	.028	6.7	35
8/7/69	1:15 p.m.	.026	6.8	21
8/7/69	6:00 p.m.	.026	7.15	34

Table 18. — Values of K for refinery clarified liquors

Date	Time	pH	K
8/4/69	3:00 p.m.	6.8	>300
8/5/69	9:30 a.m.	6.95	>300
8/5/69	2:00 p.m.	6.7	>300
8/5/69	3:00 p.m.	6.6	>300
8/5/69	3:30 p.m.	6.6	224
8/5/69	4:30 p.m.	6.7	>300
8/5/69	5:30 p.m.	6.6	>300
8/5/69	6:30 a.m.	6.6	>300
8/6/69	9:30 a.m.	6.7	>300
8/7/69	1:15 p.m.	6.65	>300
8/7/69	6:00 p.m.	6.7	>300

(5a) Comments. — On the morning of 8/5, the pH-control at the treatment station was set at 7.6. The sample of refinery treated liquor taken at 9:30 a.m. had a K value of 105, which is comparatively poor. Laboratory tests had indicated that this sugar would produce a clarified liquor of better filtering quality if the pH control were set to 7.0. Accordingly, the pH control was briefly set to 7.0 and a sample of refinery treated liquor was taken at 11:30 a.m. The value of K obtained on this sample was 40. Since this value was better than one obtained at 7.6 pH, the pH control was then set to 7.0 around 1:30 p.m.

That afternoon the clarified liquor improved in filtering quality only briefly, around 3:30 p.m. At all other times, the clarified liquor was very poor (K> 300).

Although Millipore filtration data were useful in selecting a process clarification pH, there was insufficient separation of muds from liquor in the process clarification system. It is a moot point whether this was primarily a function of the raw sugar or the process sytem.

(6) Conclusion from process studies. — The values of K in tables 7 through 18 were obtained from liquors varying from about 57 Brix to about 61 Brix. Because filterability was expressed in terms of continuous increase in resistance to flow rather than in terms of volumes collected, reduction to a standard Brix was unnecessary and data collection was expedited. The filtration data were found to be useful in selection of optimum amounts of treatment chemicals and correlated well with process control adjustments. Difficulties in process filtrations were more easily traced to either inefficient treatment or inefficient clarification.

Evaluation of raw sugars. — Most filterability methods are directed towards the evaluation of raw (or affinated) sugars. Similarities exist between the concept of this report — expressing filterability values in terms of values of K — and two other filterability methods.

(1) Plugging value test. In 1966 Faviell and Blankenbach (3) of the British Columbia Sugar Refining Company developed a filterability test based on filtering a solution of raw sugar thorugh a special filter unit until the filter is completely plugged. The filtrate weight per square inch of filter area was designated as the plugging value of the raw sugar and used as an indication of relative filterability. Although the experimental conditions are dissimilar (the British Columbia test uses a 2-sq. in. filter cloth disc and a filter aid precoat, and filters a 50 Brix solution of raw sugar at 20° C and 15 inches vacuum, the concept is similar. An abbreviated summary of the British Columbia data is presented in table 19. While Faviell and Blankenbach used a graphical solution to obtain a plugging value of 71 g./in.^{2} from their data, one might also calculate a plugging value as follows:

Table 19. — Plugging value data (after Faviell and Blankenbach (3))

V(ml.)	W(g.)	T(sec.)	T/V
25	30.8	63	2.52
50	61.6	164	3.28
75	92.4	367	4.89
100	123.2	1290	12.90

From equation 4, using the 50-ml and 75-ml data, K = 79. Using the 50-ml data and assuming the filter plugs prior to a large value of T/V (e.g., 100):

$$\frac{T_2}{V_2} - \frac{T_1}{V_1} = K \times 10^{-4}\ (T_2 - T_1)$$

$$100 - 3.28 = 79 \times 10^{-4}\ (T_2 - 164)$$

$$T_2 = 1.24 \times 10^4 \text{ sec}$$

Then $V_2 = 124$ ml.

A volume of 124 ml. corresponds to a plugging value of 76 g./in.^{2}. This calculated plugging value is somewhat higher than the one reported in (3). It should be anticipated that a plugging value calculated from early filtration data will be higher than one obtained by either extrapolating from later filtration data or filtering to zero rate since laboratory filter media have relatively short cycles.

(2) Millipore filtration of 15 Brix affination sugars. Many similarities exist between this report and the American Sugar Company filtration test (6). In the latter, affinated sugars at 15 Brix are filtered through 1.2-micron filters for 10 minutes at 22 inches vacuum and 25° C. Filtrate volumes less than 45 ml. are considered penalty grade; volumes more than 140 ml. are premium grade. Since b = 0.04 under these experimental conditions,

$$K = \left(\frac{1}{V} - \frac{b}{T}\right) \times 10^4$$

$$= \left(\frac{1}{V} - \frac{0.004}{600}\right) \times 10^4$$

$$\sim \frac{10^4}{V} \quad . \tag{10}$$

From equation 10, K>220 for a penalty grade affinated sugar and K<70 for a premium grade sugar. These values for 15 Brix syrups cannot be directly related to values of K for process liquors; however, Pearson and Amento (6) did obtain a correlation coefficent of 0.94 between filtrate volumes through Millipore filters and pounds solids through Sweetland presses.

Obviously one cannot filter a 60 Brix affinated sugar through 1.2-micron Millipore filters. The American Sugar filtration test is run at 15 Brix to dilute the insolubles. Another way to dilute insolubles would be to mix the affinated sugar with a sucrose syrup, both at 60 Brix. Table 20 summarizes filtration data of four affinated sugars diluted with sucrose syrup.

Table 20. — Filtration of mixtures of 90 percent sucrose syrup/10 percent affinated sugar syrup through 1.2-micron Millipore filters, 60 Brix, 25° C.

	Volume (ml.)			
Time (sec)	Sugar A	Sugar B	Sugar C	Sugar D
30	26	24	22	24
60	47	44	38	44
120	82	76	54	80
240	131	110	61	124
360	156	125	63	146
K	35	54	146	40
F[1]	127	83	44	113

[1] Rating by American Sugar Company test.

Although the four affinated sugars rank in the same order by both tests, the filtration data are now in a form which can be fitted by equation 2, the standard blocking equation. It is now possible to approximate the value of K of the affinated sugar from the value of K of its mixture with sucrose syrup, allowing a nominal value of K = 1 for the sucrose syrup. Each value of K is first related to a plugging value: i.e., the value of V when T/V = 100. For a sucrose syrup (K = 1), the plugging value is 10^4 ml. For the mixture of sucrose syrup and Sugar A (K = 35), the plugging value is 283 ml. Since plugging values have a reciprocal relationship,

$$\frac{1}{\dfrac{0.1}{P.V._{AFF}} + \dfrac{0.9}{P.V._{SS}}} = P.V._{mix}$$

$$\text{or,}\quad P.V._{AFF} = \frac{0.1}{\dfrac{1}{P.V._{mix}} - \dfrac{0.9}{P.V._{SS}}} \tag{11}$$

from which, for Sugar A, $P.V._{AFF}$ can be approximated as 29 ml. and K_{AFF} as 340.

Equation 11 can be used to approximate values of K of liquors for which K>300, which is the practical upper limit of the test unless one dilutes the insolubles.

SUMMARY

A method of expressing filterability as values which are not time-dependent has been described. Comparisons of the filterabilities of related laboratory and process liquors can be based on measuring the continuous increase in resistance to flow of these liquors rather than on the solids throughput obtained with a particular set of laboratory or process conditions. Although the process samples in this report concerned lime-phosphate clarification, the described method of expressing filterability probably can be adapted to any process.

ACKNOWLEDGEMENT

Appreciation is extended to Clayton Leavitt of Applied Sugar Laboratories, SuCrest Corporation, for developing the clarification procedure and for the data in Appendix B.

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APPENDIX A — CLARIFICATION PROCEDURE

Procedure	Comments
1. Add 360 grams of the affinated sugar to 240 grams of water at room temperature. Dissolve while heating to 170° F. on a hot plate.	A magnetic stirrer is not used.
2. Transfer about one-fourth of the liquor to a Waring Blendor. Turn on the blendor at low speed. Then add the remainder of the liquor. When the liquor has cooled to 155° F., add 2.45 ml. of 5 percent phosphoric acid and sufficient lime saccharate to bring to the desired pH. The reagents are added while the blendor is on; the blendor mixes an additional 60 seconds after the lime saccharate has been added.	2.45 ml. of 5 percent phosphoric acid is equivalent to 0.025% P_2O_5 on the solids basis. The amount of lime saccharate to add is predetermined for each sugar.
3. Turn off the blendor. Transfer the liquor to a 600-ml beaker. Determine the pH of the liquor; adjust the pH if necessary.	
4. Transfer the liquor to a 500-ml. aspirator bottle (Pyrex). Heat to 190° F. on a hot plate. Remove from the hot plate and let stand 15 min.	During this study, it was found that continued heating at 190° F. led to greater variance in results. It was also found that settling periods longer than 15 minutes did not affect filterability data.

5. After 15 minutes, begin draining off the liquor. Discard the first 40 ml. Drain off the next 275 ml. into a 12 fl. oz. jar. Cap and cool to 68° F. (25° C.) in a water bath. Adjust the Brix to 60 ± 0.1.

The first 40 ml. is used to rinse the tubing on the aspirator bottle. The liquor is then drawn off to within about 5 mm. of the mud level.

5 percent Phosphoric acid
10 g. 85.5 percent phosphoric acid (Baker 0260)
160 g. water

Lime Saccharate
Mix 30 grams of lime (CaO) with 395 grams of water.
Add 808 grams of 60 Brix sucrose syrup.
Mix thoroughly before each use.

APPENDIX B — VALUES OF K FOR VARIOUS P_2O_5 — pH COMBINATIONS

Raw Sugar Origin	Date	P_2O_5	pH	K
Taiwan	9/30/68	.025	7.5	50
Brazil	2/24/69	.025	6.9	298
		.025	7.2	264
		.035	6.9	85
		.040	7.5	72
Brazil	3/3/69	.010	7.2	>300
		.010	7.5	>300
Louisiana	12/9/68	.025	7.2	21
		.025	7.5	27
Louisiana	12/8/68	.010	6.9	163
		.010	7.2	133
		.025	6.9	33
		.025	7.2	34
		.025	7.5	48
		.040	6.9	9
		.040	7.2	22
		.040	7.5	38
Brazil	1/7/69	.010	7.2	264
		.010	7.5	>300
		.025	7.2	118
		.025	7.5	232
		.040	7.2	63
		.040	7.5	131
Dominican Republic	4/10/69	.010	6.9	62
		.010	7.2	130
		.010	7.5	138
		.025	6.9	22
		.025	7.2	45
		.025	7.5	48
		.040	6.9	22
		.040	7.2	16
		.040	7.5	22
Brazil	4/11/69	.025	7.0	34
		.025	7.5	67
Costa Rica	5/27/69	.025	7.0	18
		.025	7.5	20
Brazil	5/30/69	.025	7.0	53
		.025	7.5	118

DISCUSSION

R. N. POLLET: Would you care to comment on the ease, speed, and precision of the test?

J. P. SULLIVAN: The ease, speed and precision of this test are comparable to that of any test involving Millipore filtration. You just filter 500 ml through a Millipore filter apparatus for 6 minutes or for a longer time if preferred. This test is not presented primarily from the point of view of improving ease, speed or precision over tests presently available. Rather this test eliminates membrane standardization and, in certain cases, standardization of test liquors, thereby contributing to ease and speed.

W. L. REED: Have you done any tests on the same materials at different pH? I notice quite a few variations, on a pH scale, but they were presumably not on the successive liquors.

J. P. SULLIVAN: Our laboratory tests were done in accordance with SuCrest's Brooklyn refinery, which usually clarifies as closely as possible to 7.0 pH, extensively monitored by Auto-Analyzers. The refinery clarifies occasional raw sugars up to 7.6 pH because of other considerations, but our testing indicated that 7.0 was a better clarification pH, in terms of filterability of the clarified liquor.

W. L. REED: So 7.0 is your best bet?

J. P. SULLIVAN: We tested 50 or 60 raw sugars in the laboratory and on every one, with one exception, 7.0 pH was better than 7.5 pH. The exception was the Fiji raw sugar mentioned in this report, which was very good at both pH's, but slightly better at 7.5 pH.

QUANTITATIVE MEASUREMENT OF SUGARS BY GAS-LIQUID CHROMATOGRAPHY

by

Violeta S. Velasco, M. Heisler, and J. F. Dowling
Corn Industrial
Yonkers, N. Y.

(Presented by Violeta S. Velasco)

ABSTRACT

The various methods applicable to the measurement of dextrose, levulose, and sucrose by gas-liquid chromatography (GLC) have been investigated in regard to reagents used in preparing trimethylsilyl derivatives, reaction rates, and internal standards. A precision of 0.5 percent is attainable. GLC can be used to measure colorants, but separation from most of the sugar and concentration is necessary.

INTRODUCTION

The gas-liquid chromatographic (GLC) method for the separation of silyl sugar derivatives was introduced in 1960 and has indicated an interesting future in the sugar industry as an analytical tool. Gas-liquid chromatography is basically a process by which a mixture is separated into its components by a moving gas phase over a nonvolatile liquid coated on an inert solid support. When a sample is injected into the injection port, it is swept by the carrier gas, first evaporating to form a vapor. As the vapor moves through the column, it is dissolved in and revaporized from the liquid phase. The components having the greater solubility in the liquid phase are retarded in their passage. Since different substances vary in their solubility, they are separated by their different rates of progress through the column. As they are eluted at the far end of the column, they appear one after the other in the gas stream, the fastest first and the slowest last. The separated components along with the carrier gas pass through the detector, which senses and measures the components present and sends a signal to the recorder. The signal obtained is recorded in the form of a peak which is proportional to the concentration of the component.

The lack of volatility of carbohydrates has been overcome by converting them to volatile polytrimethylsilyl ethers.[1] Figure 1 shows the chemistry involved in the derivatization process. The trimethylsilyl (TMS) group is readily introduced in the sugar molecule by replacement of the hydrogen atom in the hydroxyl group. The reaction takes place in pyridine, using hexamethyldisilazane (HMDS) as the major silylating agent. Reports have indicated that maximum yield could be attained if trimethylchlorosilane (TMCS),[1] or trifluoroacetic acid (TFA) is employed as a catalyst.[2]

For quantitative work, an internal standard is necessary. An internal standard is a pure compound added to the mixture to be analyzed to compensate for fluctuation in column conditions and sensitivity. Alexander and Garbutt[3] used sorbitol in the determination of dextrose in corn syrups as the compound elutes between α-dextrose and β-dextrose. Corn Industries Research Foundation[4] found phenyl-β-glucoside to be a suitable internal standard, since its TMS derivative is eluted between dextrose and sucrose. Figure 2 shows the structure of these two compounds.

We attempted to adopt these methods to the quantitative analysis of samples most often encountered in the Refined Syrups and Sugars Technical Service Department. However, several

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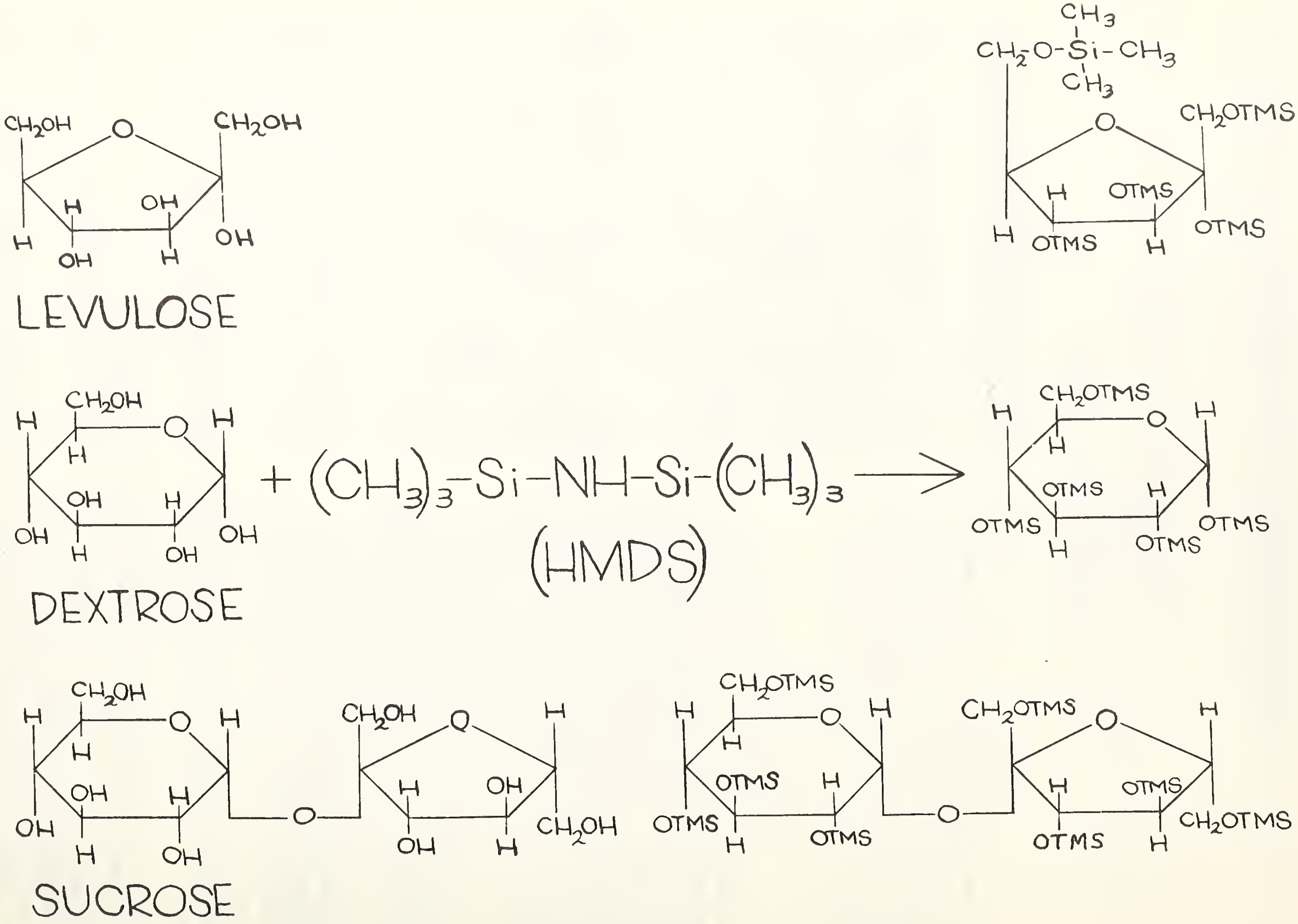

$+ (CH_3)_3-Si-NH-Si-(CH_3)_3 \longrightarrow$

Figure 1. — Chemistry involved in silylation of sugars.

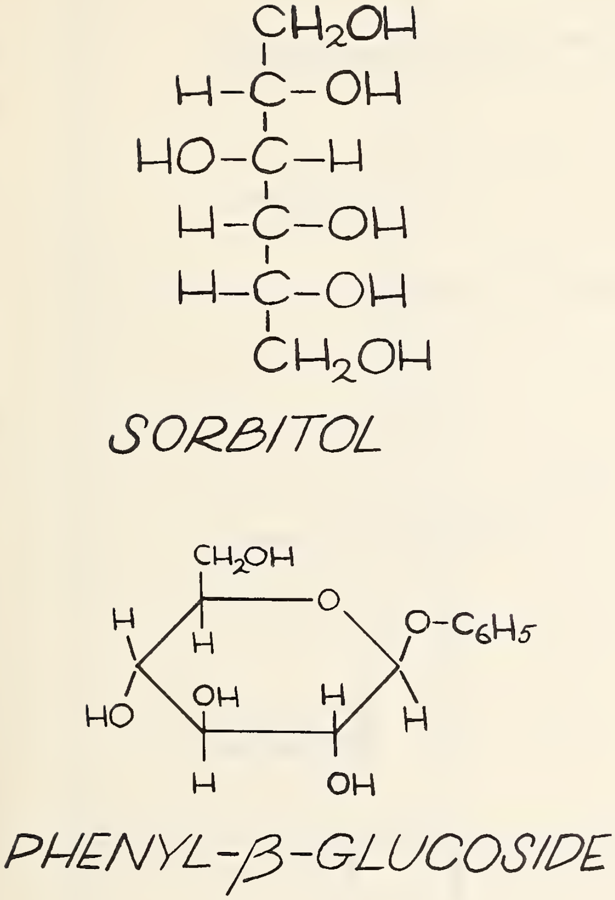

Figure 2. — Internal standards.

difficulties were experienced, so that satisfactory quantitation of the sugars was not obtained. This has led us to investigate further these existing methods in application to our major finished products. This paper is intended as a progress report to describe the present state of methods development in our own department. The primary objectives are as follows:

1. To determine levulose, dextrose, and sucrose quantitatively in sugar syrups.

2. To compare the effects of TMCS and TFA on silylation reaction.

3. To find the most suitable internal standard for the above-mentioned sugars.

4. To evaluate the various methods of silylation and determine reproducibility. One of the other applications of GLC to the sugar industry could be its use in measuring colorants. Initial data on the separation and qualitative determination will also be discussed.

EVALUATION OF METHODS FOR SILYLATION

Among the various methods of derivatization, we selected three direct methods: (1) HMDS-TMCS method, (2) Trisil-Z, and (3) HMDS-TFA method. Aqueous solutions of high purity sugars were prepared containing not less than 50 percent solids. Individual sugars were derivatized and analyzed by GLC methods. Peak areas were measured, using an accurate ruler, by the height X width at half-height method. Response factors (K value) were calculated as follows:

$$K = \frac{\text{Total peak area of sugar}}{\text{Peak area of internal standard}} \times \frac{\text{Weight of internal standard}}{\text{Weight of sugar}}$$

HMDS-TMCS method. The silylation of sugar using 4 ml. HMDS and 2 ml. TMCS was conducted at room temperature. The solutions became cloudy on addition of trimethylchlorosilane (TMCS) presumably due to precipitation of NH_4Cl[5]. Conflicting theories were published as to the function of TMCS. Some investigators regarded TMCS as a catalyst, since it increases the rate of silylation; others call it an effective silyl donor because it takes part in silylation and is partially consumed as NH_4Cl is formed. The samples were analyzed by GLC for 4 consecutive days, and the K values are plotted in figure 3. The K values increased markedly on the second day, perhaps due to completion of the reaction. The TMS derivatives seemed to be stable after the second day.

Trisil-Z (n-trimethylsilylimidazole in pyridine). This method involved the direct addition of 1 ml. of the prepared reagent to 10 mg. of sample.[5] The reaction mixture was allowed to stand for 15 minutes before injection in GLC Derivatization of levulose alone resulted in multipeaks as shown in Figure 4: 1) a major levulose peak, 2) a minor peak with similar retention time as α-dextrose, and 3) another minor peak which was eluted after α-dextrose. The major levulose peak was asymmetrical which might be an

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[5] Karr, J., and Norman, L. A. 1970. Presented to the 16th General Meeting, Amer. Soc. Sugar Beet Technol.

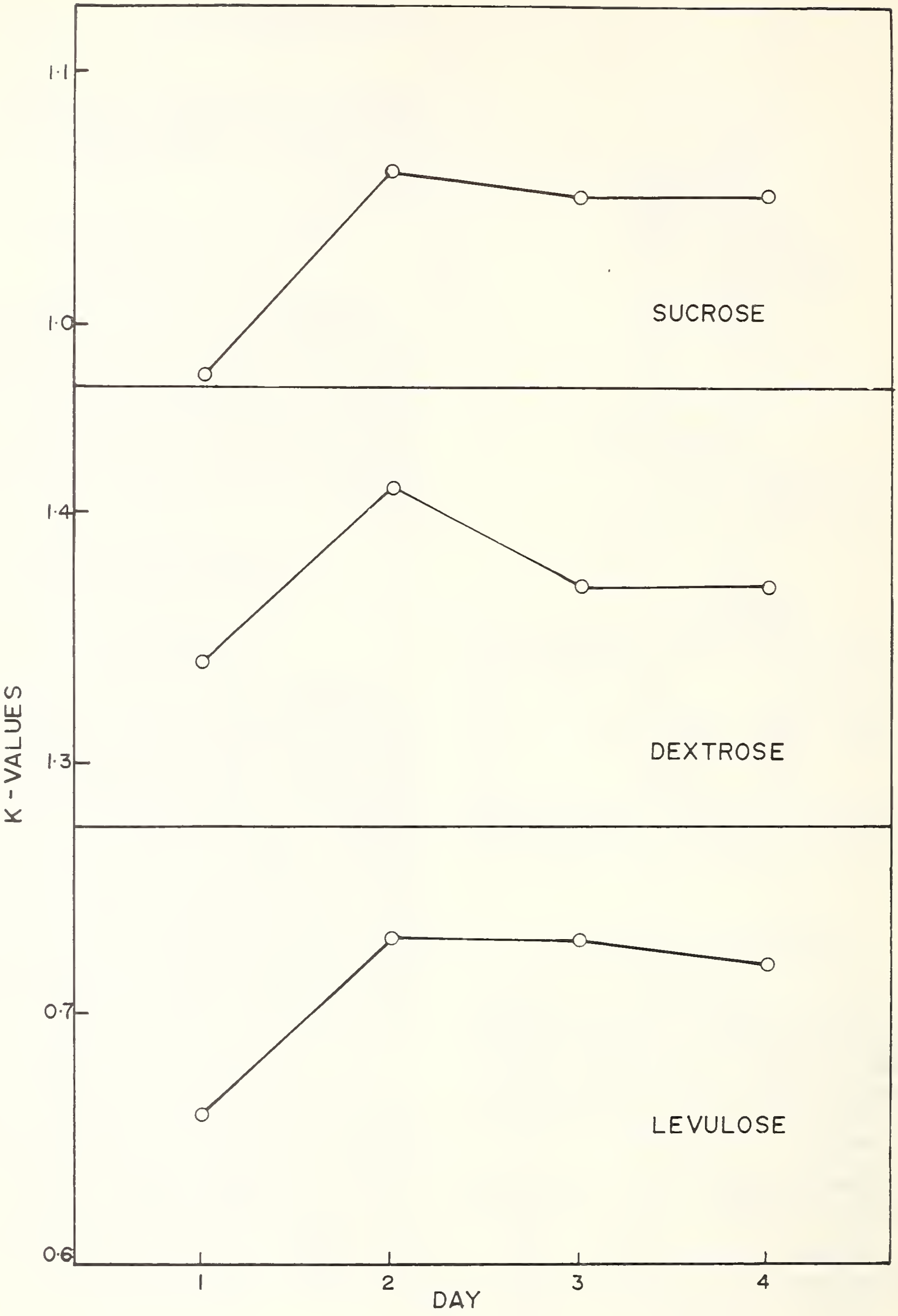

Figure 3. — K value derivatized with HMDS and TMCS at room temperature.

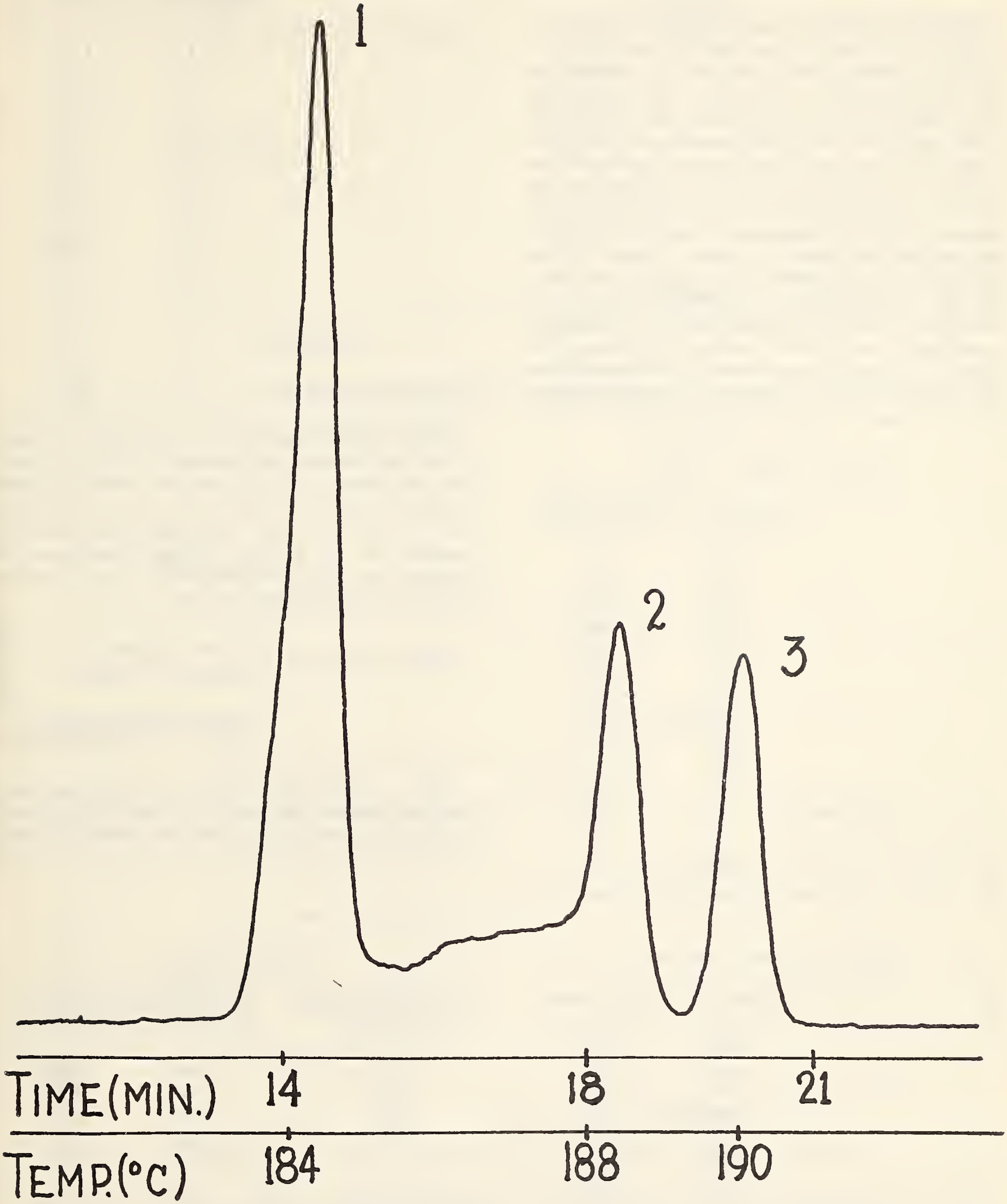

Figure 4. — Typical chromatogram of levulose derivatized with N-trimethylsilylimidazole (trisil-Z).

indication that the silylation reaction was not complete.

HMDS-TFA. The silylation of sugar samples was conducted according to the method used by Corn Industries Research. This consisted of warming the sugar-pyridine solution in a 65° to 70°C. water bath before derivatization. The silylating agent was 5 ml. HMDS and 0.5 ml. TFA. This eliminated the formation of NH_4Cl and yielded a clear colorless solution of the derivative. The mixture was then refluxed for 15 minutes. The TMS derivatives were tested by injecting samples in GLC for 4 consecutive days. K values of the three sugars were plotted as shown in figure 5. This indicated that derivatization reactions were completed by this method almost immediately. Since the HMDS-TFA method exhibited the most complete derivatization and yielded constant K values, this method of silylation was chosen for further studies. The average K values obtained by this method are shown in tables 1, 2 and 3.

Table 1. — K value — levulose

	SORBITOL	GLUCOSIDE
	0.71	1.11
	.72	1.10
	.69	1.08
	.70	1.09
	.68	1.12
	.71	1.14
	.70	1.12
	.71	1.07
	.68	1.11
	.70	—
AVERAGE	.70	1.10
AVERAGE DEVIATION	.01	.02

Table 2. — K value — dextrose

	SORBITOL	GLUCOSIDE
	0.83	1.37
	.88	1.37
	.83	1.28
	.85	1.33
	.85	1.27
	.87	1.36
	.85	1.33
AVERAGE	.85	1.33
AVERAGE DEVIATION	.01	.03

Table 3. — K value — sucrose

	SORBITOL	GLUCOSIDE
	0.71	1.12
	.74	1.09
	.71	1.08
	.70	1.10
	.71	1.11
	.71	1.10
	.69	1.12
	.68	1.09
	.70	1.11
	.68	1.09
	.71	1.08
	.70	1.11
AVERAGE	.70	1.10
AVERAGE DEVIATION	.01	0.01

When sorbitol is used as internal standard, K values of levulose, dextrose, and sucrose are 0.70, 0.85, and 0.70, respectively. On the other hand, when glucoside is used, K values of levulose, dextrose, and sucrose are 1.10, 1.33, and 1.11, respectively, with average deviation of .01 to .03. Attempts were made to calculate the sugars recovered, using these K values according to the following formula:

$$\text{Weight of sugars} = \frac{\text{Peak area of sugars}}{\text{Appropriate K values}} \times \frac{\text{Weight of internal standard}}{\text{Peak area of internal standard}}$$

Table 4 shows the analyses of five analytically prepared standard solutions of levulose. Both sorbitol and glucoside seemed to be a suitable internal standard for levulose. Table 5 shows the recovery of dextrose.

Table 4. — Levulose

MG. IN STANDARD SOLUTION	MG. RECOVERED	
	SORBITOL	GLUCOSIDE
4.04	4.04	4.02
4.69	5.03	5.01
8.55	8.39	8.78
9.81	9.82	9.76
17.10	16.84	16.91
AVERAGE DEVIATION	.20	.15
AVERAGE PERCENT ERROR	2.22	1.67

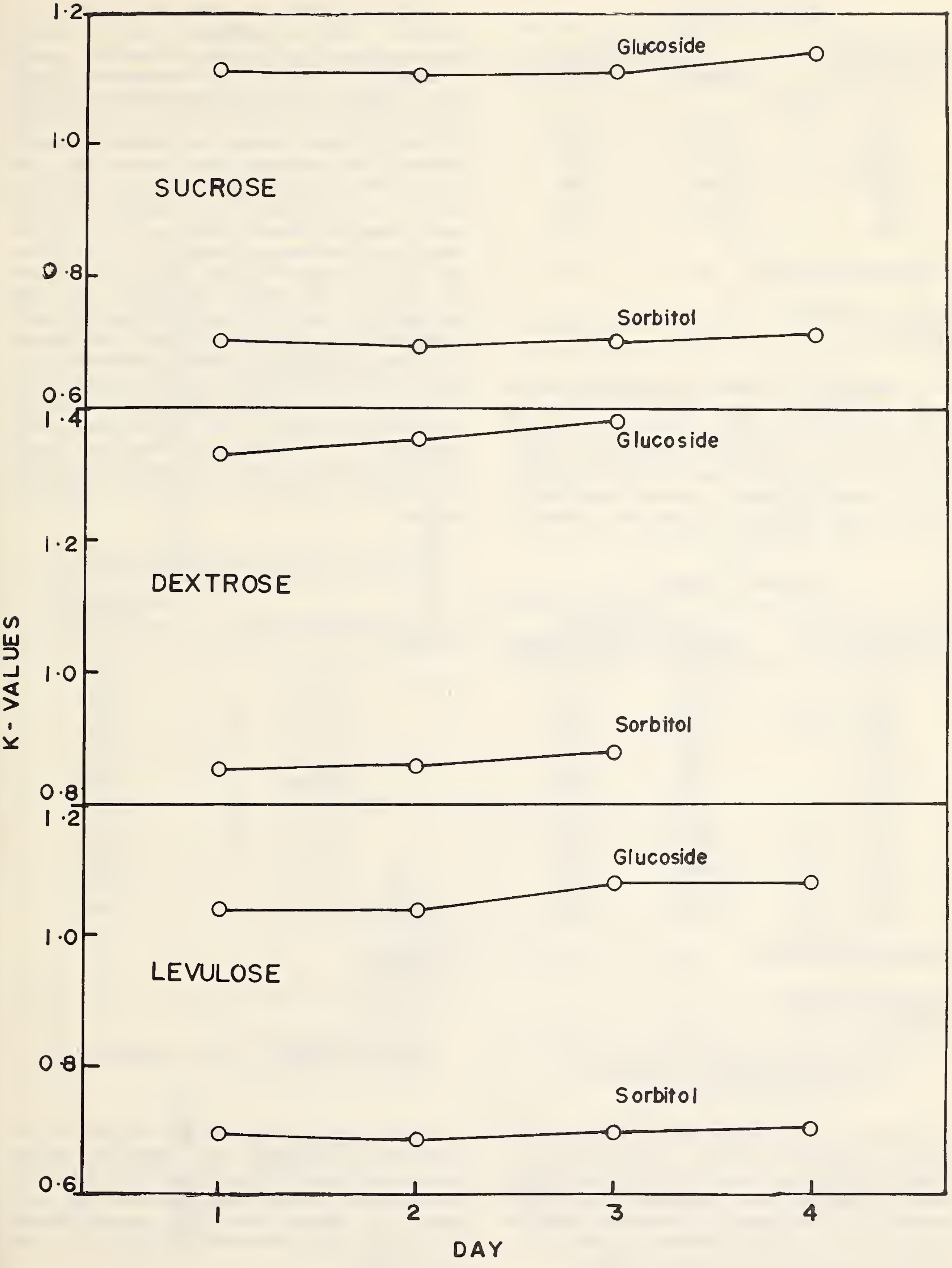

Figure 5. — K value derivatized with HMDS and TFA.

Table 5. — Dextrose

MG. IN STANDARD SOLUTION	MG. RECOVERED SORBITOL	MG. RECOVERED GLUCOSIDE
2.26	2.27	2.40
4.06	4.13	4.14
5.54	5.76	6.73
5.85	5.98	5.98
6.10	6.05	5.85
9.58	9.62	9.57
AVERAGE DEVIATION	.09	.30
AVERAGE PERCENT ERROR	1.62	5.38

Better accuracy was obtained using sorbitol with an average deviation of ±.09. However, it could be pointed out that one of the results of the analysis using glucoside was rather high, which makes the large average deviation of ±.30. Table 6 shows the analyses of 11 standard solutions of various quantities of sucrose. There appears to be not much difference between sorbitol and glucoside results.

Table 6. — Sucrose

MG. IN STANDARD SOLUTION	MG. RECOVERED SORBITOL	MG. RECOVERED GLUCOSIDE
2.37	2.46	2.43
2.61	2.46	2.43
3.23	3.08	3.26
5.41	5.37	5.31
5.99	6.04	5.89
6.42	6.46	6.34
8.31	8.99	8.56
9.11	8.70	9.02
10.16	10.30	10.08
10.16	10.29	9.97
18.22	18.05	17.95
AVERAGE DEVIATION	.19	.13
AVERAGE PERCENT ERROR	2.55	1.74

REPRODUCIBILITY OF SUGAR DETERMINATIONS

To ascertain the reproducibility of the method described, analytically prepared standard mixtures of levulose, dextrose, and sucrose were analyzed by five analysts in two separate laboratories. The percent composition of the mixture was calculated, based on the quantity of the sample weighed out. Figure 6 is a typical chromatogram of the mixture of sugars.

In the quantitation of dextrose in the presence of levulose, certain difficulties arose. A typical chromatogram of levulose alone is shown in figure 7. Comparing fig. 6 to fig. 7, it is evident that a minor peak, possibly an anomer, emerges which, if dextrose were present, would overlap with the α-dextrose peak. A literature search revealed no available information regarding this overlapping peak. Reports were made that in hot pyridine anomerization of sugars may occur[1]. To verify this, TMS derivatives of levulose were prepared by dissolving in cold pyridine or by first heating the pyridine-sugar solution in a water bath at 65° to 70°C. before silylation. The results are shown in table 7. We found that heating the sugar sample-pyridine solution before derivatization reduced anomerization to a great extent, from 11 to 6 percent. The ratio of Levulose 2/Levulose 1 was constant in all samples over the range of 4.54 to 8.52 percent with an average value of 5.95 percent. By subtracting 6 percent of the area of Levulose 1 from the area of α-dextrose, quantitation of dextrose was satisfactory. Typical results are shown in table 8. Note that heating the sample-pyridine solution causes about 1.5% increase in levulose.

Table 7. — Ratio of Levulose 2 to Levulose 1

	ROOM TEMPERATURE	WATER BATH 65° to 70°C.
	10.62	6.57
	10.51	6.47
	12.49	5.91
	10.64	4.73
	11.49	8.52
	10.25	4.54
	10.56	6.37
	12.74	6.18
	10.45	5.12
	10.43	5.13
AVERAGE	11.02	5.95
AVERAGE DEVIATION	.73	.85

$$\frac{\text{AREA LEVULOSE 2}}{\text{AREA LEVULOSE 1}} \times 100 = \text{PERCENT } L_2/L_1$$

Tables 9 and 10 show the data obtained for two standard sugar mixtures when tested by the five analysts. The mean and the average deviation from the true values for levulose and dextrose were fairly good, being of a magnitude of about 0.5 percent. However, the sucrose average deviation was large and in both cases negative.

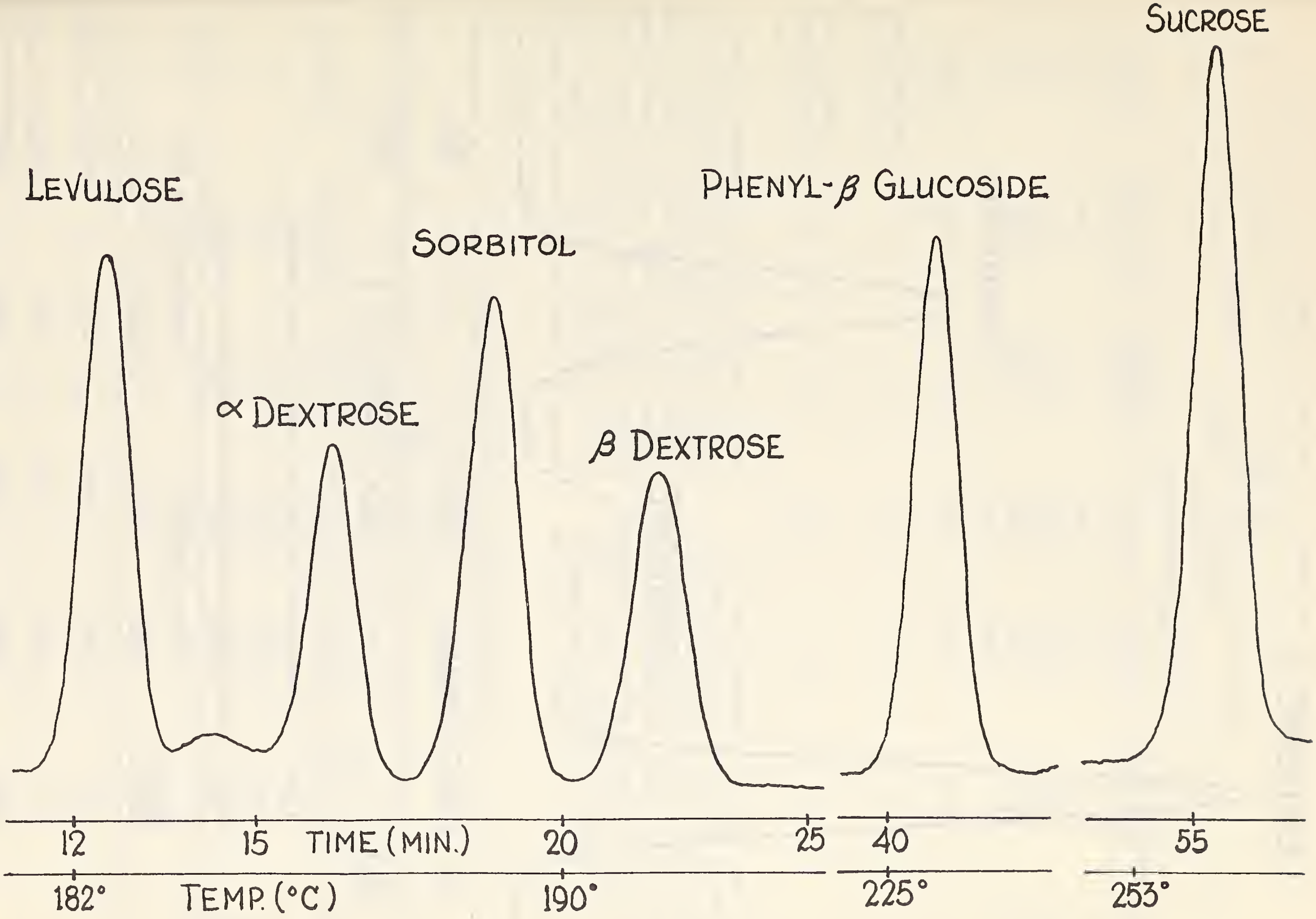

Figure 6. — Chromatogram of a mixture of levulose, dextrose, sucrose, and internal standards.

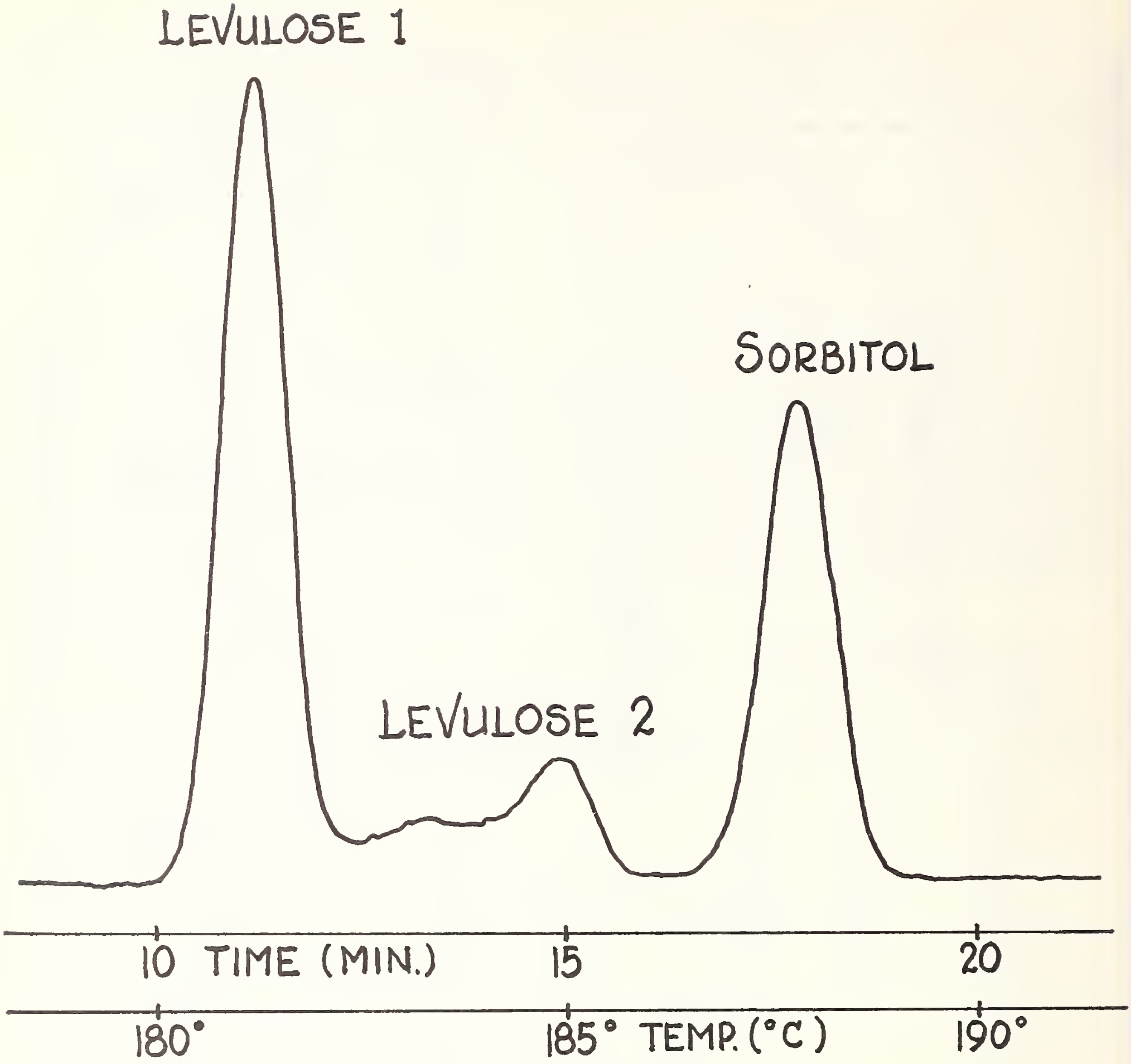

Figure 7. — Chromatogram of levulose and sorbitol as internal standard.

Table 8. — Effect of heating sample—pyridine solution before derivatization

Sugar	Standard solution	Room Temperature		Water Bath (65° to 70°C.)	
		Sorbitol	Glucoside	Sorbitol	Glucoside
Levulose	19.90	18.81	18.66	20.28	20.11
Dextrose	19.95	21.17	21.05	20.37	20.34
Sucrose	26.40	24.49	24.07	24.09	23.73

Table 9. — Reproducibility of sugar determinations

Mixture No. 1
Levulose = 20.03 percent Dextrose = 20.10 percent
Sucrose = 26.82 percent

	PERCENTAGE IN SAMPLE					
	SORBITOL			GLUCOSIDE		
ANALYST	LEVULOSE	DEXTROSE	SUCROSE	LEVULOSE	DEXTROSE	SUCROSE
A	20.00	20.45	26.60	19.91	20.50	26.30
B	19.58	20.80	21.63	20.86	22.24	22.85
C	20.31	19.76	19.47	21.69	22.69	20.60
D	20.83	20.11	25.73	18.92	18.34	23.16
E	21.21	20.72	24.66	20.06	19.70	23.13
MEAN	20.39	20.37	23.62	20.29	20.69	23.21
Average deviation (From true value)	.55	.40	3.20	.75	1.46	3.61
Average deviation (From the mean)	.51	.35	2.45	.79	1.42	1.24

Table 11 compares the average deviation of mean sugar content found for various samples when analyzed by five chemists. For the three samples which were heated prior to derivatization, the levulose and dextrose had an average deviation of +.34 and +.45 percent sugar from the true value. For the samples that were not heated, the levulose average deviation became −0.77 percent and dextrose +.96 percent. This difference was attributed to the difference in the ratio of Levulose 2/Levulose 1 (L2/L1) due to heating. Thus, this points out the importance of accounting for the levulose peak underneath the α-dextrose peak. This could be accounted for by making the correction for the percent L2/L1 without heating; however, since this percent is decreased by heating, it was felt that heating would be a better method. The less Levulose 2 present, the more accurate is the determination of levulose and dextrose.

Table 10. — Reproducibility of sugar determinations
Mixture No. 2
Levulose = 20.00 percent Dextrose = 20.00 percent
Sucrose = 26.79 percent

	PERCENTAGE IN SAMPLE					
	SORBITOL			GLUCOSIDE		
ANALYST	LEVULOSE	DEXTROSE	SUCROSE	LEVULOSE	DEXTROSE	SUCROSE
A	19.85	20.02	24.70	20.08	20.40	24.48
B	20.11	21.76	26.37	20.58	22.18	26.78
C	19.23	20.33	25.69	19.28	20.44	25.64
D	21.14	20.54	26.59	19.24	18.42	23.59
E	21.06	20.74	27.05	18.91	18.70	24.06
MEAN	20.28	20.68	26.08	19.62	20.03	24.91
Average deviation (From true value)	.65	.68	.81	.65	1.18	1.88
Average deviation (From the mean)	.66	.47	.71	.57	1.17	1.04

Table 11. — Average deviations for sugars

Samples	Sorbitol			Glucoside		
	Levulose	Dextrose	Sucrose	Levulose	Dextrose	Sucrose
HEATED						
1	+.36	+.26	-3.20	+.26	+.59	-3.61
2	+.28	+.68	- .71	-.38	+.03	-1.88
3	+.38	+.42	-2.31	+.21	+.36	-2.67
Average	.34	.45	2.07	.28	.33	2.72
UNHEATED						
1	-1.09	+1.22	-1.91	-1.34	+1.10	-2.43
2	- .98	+ .94	-1.59	-1.63	+ .31	-2.73
3	- .23	+ .73	-2.87	- .37	+ .62	-3.25
Average	.77	.96	2.12	1.11	.68	2.80

The sucrose mean was consistently below the true sucrose content of the mixture by about 2.0 percent. This large deviation may be due to several factors, namely: (1) selectivity of reactions — silylation of sucrose (disaccharide) may be more difficult in the presence of monosaccharides; (2) experimental errors such as weighing and pipetting techniques (as the analyses were repeated, better precision was obtained); (3) other factors which affect the rate of reaction; and (4) possible error in sucrose K value.

Another error in determining the sugar content is that associated with the measurement of peak areas. While evaluating errors, it was noted that there was a discrepancy in area measurements by various analysts. The height × width at half-height method was being used to measure peak areas. Some of the analysts were using the peakometer, which is calibrated in tenths of a mm. Others were using a ruler calibrated in 0.5 of a mm. To determine the error, five chromatograms were Xeroxed and measured by all five analysts. Initial data indicated a big difference in area between analysts using the peakometer and those using the ruler. It was decided that all analysts should use the ruler since it has greater accuracy.

Table 12 shows the range (difference between high and low) for the peak area measurements by the five analysts for the five chromatograms. From the limited data, one could expect a range of 0.50 mm^2 in area measurements for a single chromatogram. To minimize the error in sugar determination, it was felt that three injections for each sample were necessary. With this in mind, the areas from the three chromatograms measured by the analysts were averaged, and the ranges of these average peak areas are shown in table 13.

Table 12. — Range for peak area measurements by five analysts

	RANGE IN MM^2						
Chromatogram	Levulose	α-Dextrose	β-Dextrose	Sucrose	Sorbitol	Glucoside	Average
1	.81	.11	.35	.23	.45	.06	.37
2	.11	.43	1.08	.37	.47	.29	.46
3	.61	.28	.57	.30	.70	.77	.54
4	.16	.23	.65	.46	.91	1.03	.57
5	.28	.22	.31	.32	.35	.37	.32

Table 13. — Range for average peak area measurements of three chromatograms by five analysts

	Levulose	α-Dextrose	β-Dextrose	Sucrose	Sorbitol	Glucoside	Average
Average Chromatograms 2, 3, 4	.23	.30	.34	.50	.53	.69	.43
Average (less one) analyst							
Chromatograms 2, 3, 4	.16	.18	.14	.33	.42	.30	.26
Chromatograms 3, 4, 5	.24	.24	.30	.25	.26	.34	.27

In doing this, it was noted that one analyst was consistently low, indicating some error in his technique of measurement. By eliminating this analyst's area measurement, the average range was decreased 40 percent. By replacing the data for Chromatogram 2 with that of Chromatogram 5, a new average for Chromatograms 3, 4, and 5 was obtained, which showed an almost identical average range of 0.27, compared to 0.26 from Chromatograms 2, 3, and 4.

Table 14. — Range and average deviation for percent sugars calculated from areas measured by five analysts

Area averaged	Levulose percent	Dextrose percent	Sucrose percent
Chromatograms 2, 3, and 4			
Average content	20.75	20.90	25.20
Range	.43	.60	.88
Average deviation	.14	.17	.25
Chromatograms 3, 4, and 5			
Average content	20.09	20.72	25.15
Range	.28	.10	.68
Average deviation	.09	.03	.19

To estimate the error in determining sugar content, the average areas obtained from the two sets of chromatograms were used to calculate percent sugars for each analyst. The average percent sugar (table 14) was calculated by averaging the data obtained by the four analysts. Because of the error in measurements of peak areas by various analysts, an average deviation of not less than 0.20 percent sugar and a range of less than 0.70 percent sugar can be expected.

By establishing more exact means of measuring height, and width, and drawing the base line, and improving analysts' techniques, this deviation could be further reduced. Also, the application of a disc integrator for the measurement of peak areas should reduce this error.

SUGAR COLORANTS

The Cane Sugar Refining Research Project[6] reported on the separation of various sugar colorants by high voltage paper electrophoresis at their 1968 technical sessions, and in 1970,[8] the identification of these colorants. Four of the compounds identified were chlorogenic acid, caffeic acid, ferulic acid, and sinapic acid. All of these compounds are derivatives of, or closely related to, cinnamic acid; and the trimethylsilyl ethers of these compounds have been previously prepared by various methods.[7]

We were able to prepare the derivatives by using either TFA or TMCS with HMDS. We attempted to speculate on the structure of silylated sugar colorants, as shown in figure 8. The four colorants were readily separated on the SE-52 column, under similar conditions used for sugar analyses (figure 9).

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[6] Farber, L., McDonald, E. J., and Carpenter, F. G. 1969. Separation of colorants from cane sugar. Proc. 1968 Tech. Sess. Cane Sugar Refin. Res., 85-104.

[7] Pierce, A. 1968. Silylation of Organic Compounds, Pierce Chemical Co., pp. 186-189.

[8] Farber, L, and Carpenter, F. G. 1971. Identification of sugar colorants. These proceedings pp. 145-156.

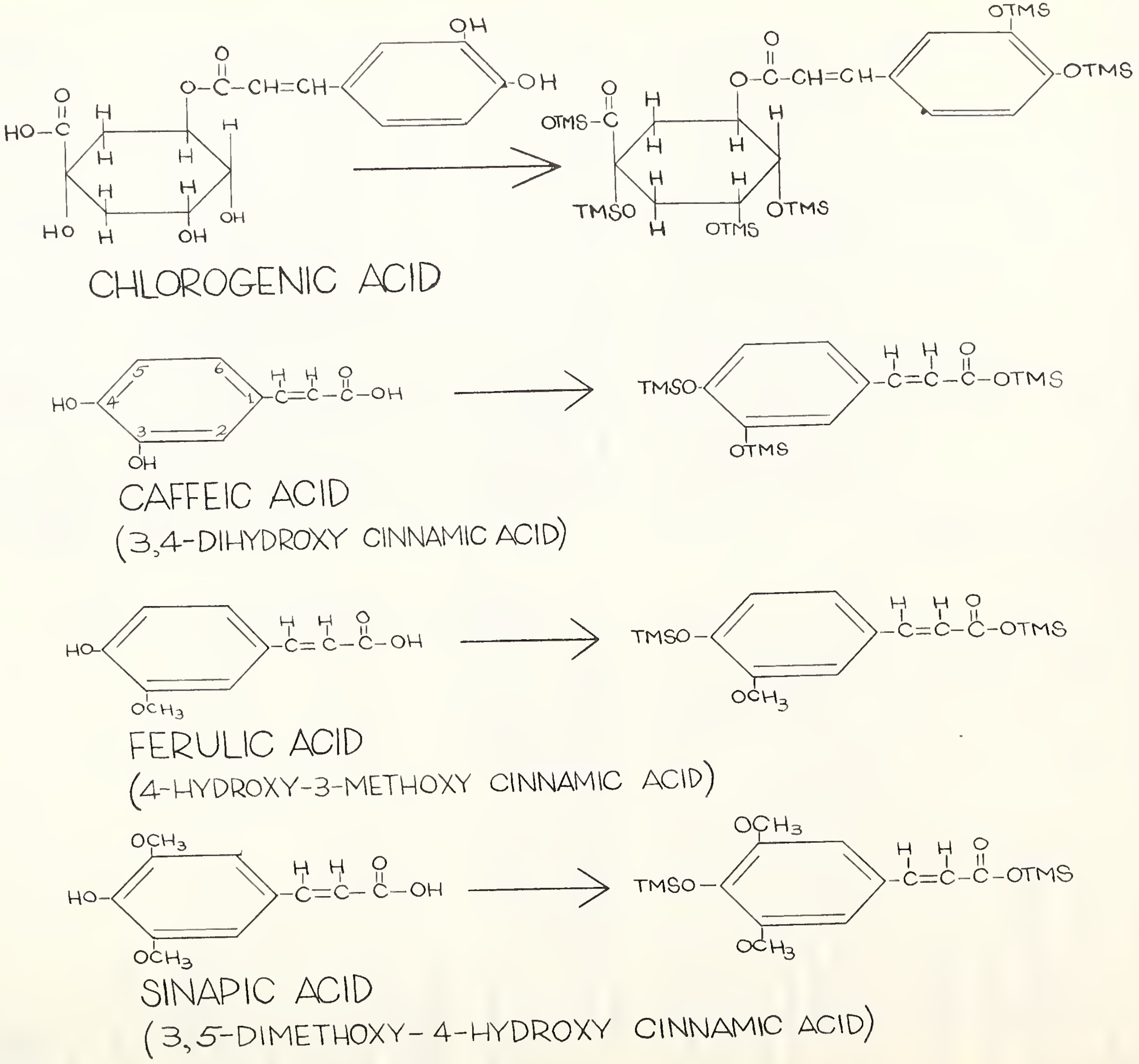
CHLOROGENIC ACID
CAFFEIC ACID
(3,4-DIHYDROXY CINNAMIC ACID)
FERULIC ACID
(4-HYDROXY-3-METHOXY CINNAMIC ACID)
SINAPIC ACID
(3,5-DIMETHOXY-4-HYDROXY CINNAMIC ACID)
OTMS
TMSO
OCH3

Figure 8. – Probable structures of silyl derivatives of sugar colorants.

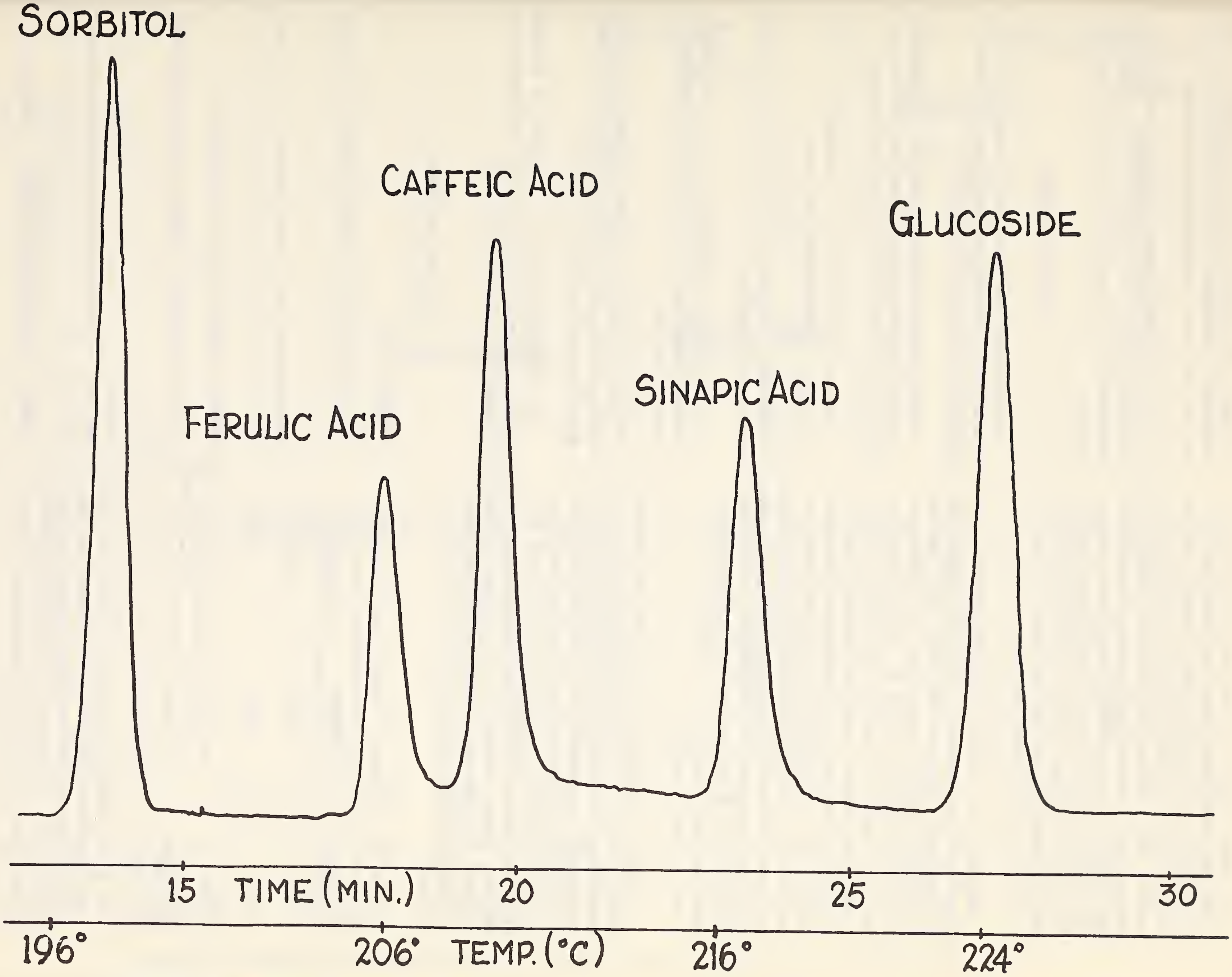

Figure 9. — Separation of colorants and internal standards in SE-52 column, programmed at 170° to 270° C. at 2°/min.

The order in which the acids were eluted from the column was: ferulic acid, caffeic acid, sinapic acid, and chlorogenic acid. Thus a hydroxy addition on the benzene ring of cinnamic acid has a greater effect on retention time of the derivatives than the addition of a methoxy group. However, in the case of sinapic acid, the addition of two methoxy groups has a greater effect on retention time than a single hydroxy group. From this, one should be able to predict the elution order for other cinnamic acid derivatives that are no doubt associated with sugar colorants.

Samples which contained dextrose, levulose, and sucrose were also analyzed on the SE-52 column; and the retention times were such that there was no interference from the sugars (figure 10). Chlorogenic acid had a retention time of 57 minutes, eluting at 284°C. It would be expected that higher molecular weight sugar colorants would not be eluted from this particular column. The sugar colorants were, therefore, separated on a JXR column which has been shown to be capable of separating trisaccharides. The chlorogenic acid was eluted within 30 minutes at 238°C. under the conditions outlined in the experimental section, but α-dextrose and ferulic acid have very similar retention times and made separation on this column almost impossible (figs. 11 and 12).

K values were calculated using the two internal standards (table 15). It was not intended that either of these internal standards be recommended for use in quantitating sugar colorants, but mainly for estimation of the response factors of these compounds to a flame ionization detector. It appears that there could be a correlation between the response and the number of methoxy groups attached to the benzene ring of cinnamic acid, since the K values indicate that caffeic acid has the highest response, ferulic next, and sinapic the least.

Table 15. — Estimated K values for sugar colorants

Acid	Sorbitol	Glucoside
Ferulic	0.367	0.538
Caffeic	.530	.747
Sinapic	.251	.351
Chlorogenic	.474	.676

It is not feasible at this time to expect that one could derivatize a sugar sample and measure the sugar colorants directly. They are present in such a minute quantity that concentration of the colorants will be necessary along with separation from the mass quantity of sugar. One should be able to concentrate these colorants by extraction with a suitable solvent or by elution from an ion exchange or carbon column.

Once the colorants are concentrated, then a GLC method should be suitable for quantitative measurement of a great number of the compounds present.

CONCLUSIONS

Levulose has two peaks. One is under α-dextrose. Heating helps reduce the second peak to about 6 percent of the major levulose peak.

Method presently discussed with TFA is capable of measuring individual sugars within 0.5 percent error. Dextrose and levulose have less error than sucrose.

Reaction of TMCS is not complete at room temperature until after about 24 hours.

Reaction of levulose with Trisil Z gives three peaks under normal condition.

In quantitative determination of sugar content, means of measuring peak areas should be established to minimize the errors.

Excellent separation of TMS derivatives of ferulic, caffeic, sinapic, and chlorogenic acid were obtained using SE-52 column at 170° to 300°C.

Gas chromatography can be applied to measure colorants; however, separation from a mass quantity of sugar and concentration is necessary.

EXPERIMENTAL

Reagents

Hexamethyldisilazane — Pierce Chemical Co., Rockford, Ill.

Trifluoroacetic Acid — Pierce Chemical Co., Rockford, Ill.

Pyridine — Fisher Scientific Co. Springfield, N. J.

D-levulose — Matheson, Coleman, and Bell, Rutherford, N. J.

Sucrose)
Dextrose) — National Bureau of Standards, Washington, D.C.

Sorbitol — Eastman Organic Chemical, Rochester, N. Y.

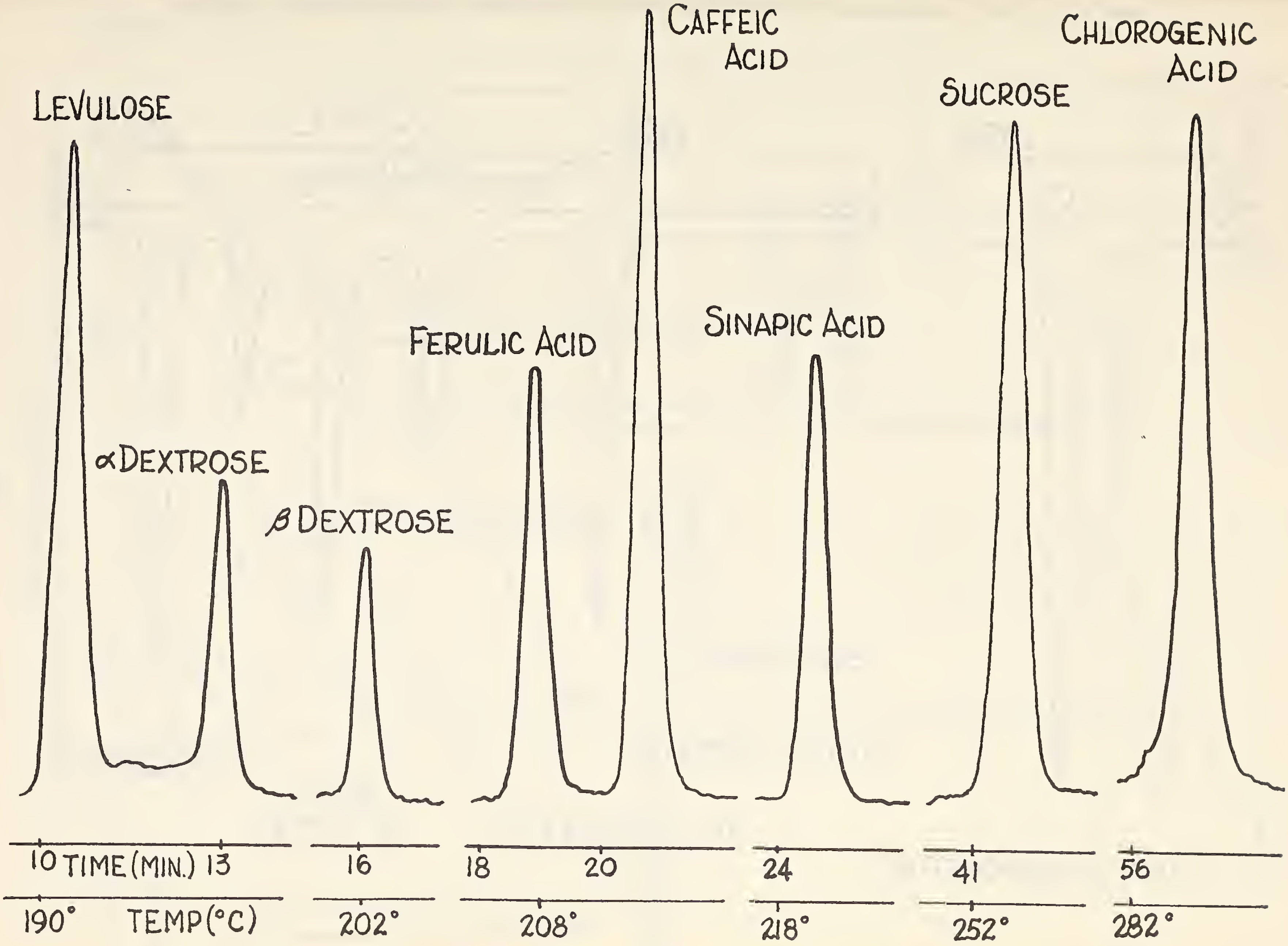

Figure 10. — Separation of colorants and sugars in SE-52 column, programmed at 170° to 300° C. at 2°/min.

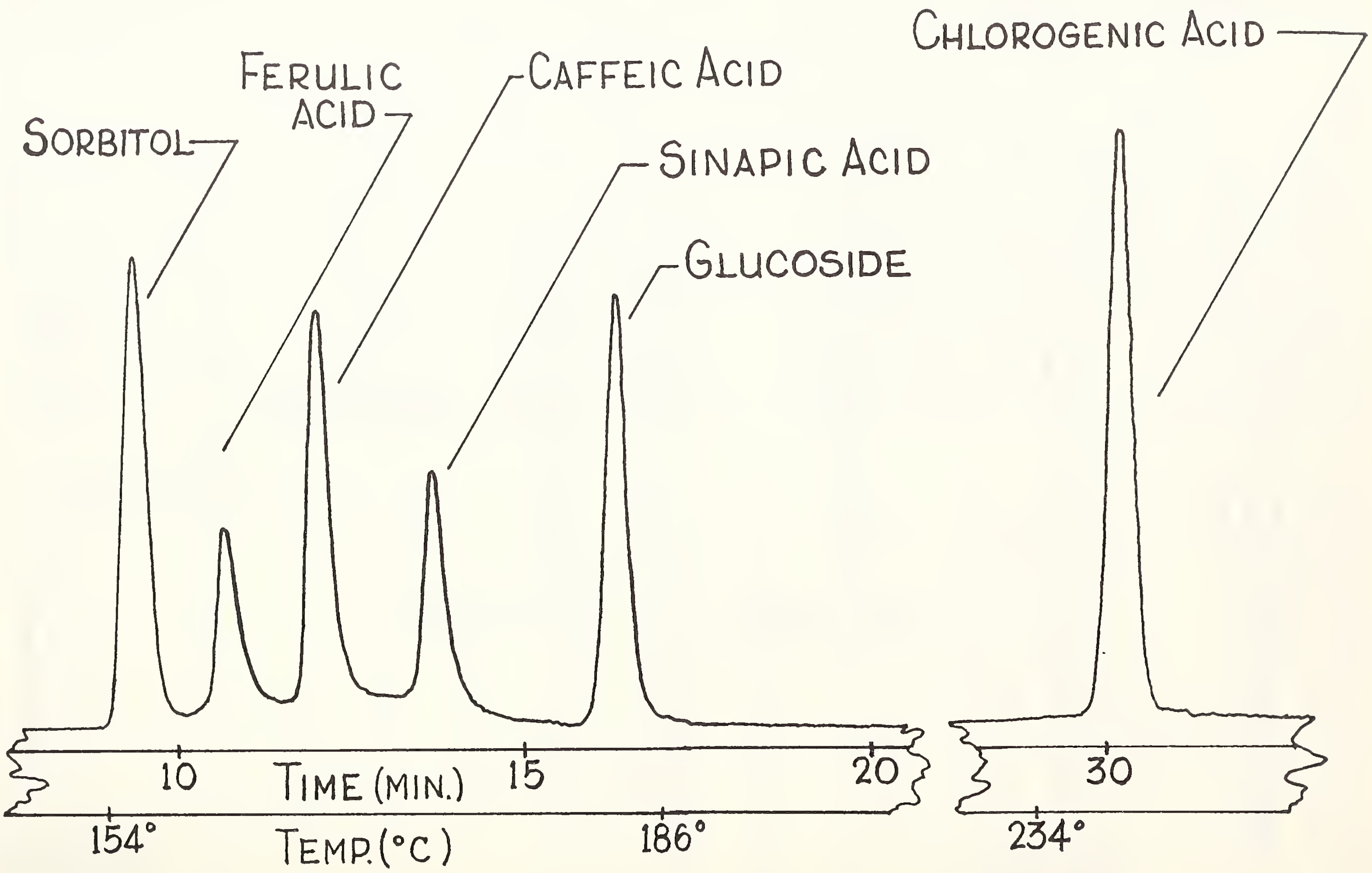

Figure 11. — Separation of colorants and internal standards in JXR column programmed at 118° to 240° C. at 4°/min.

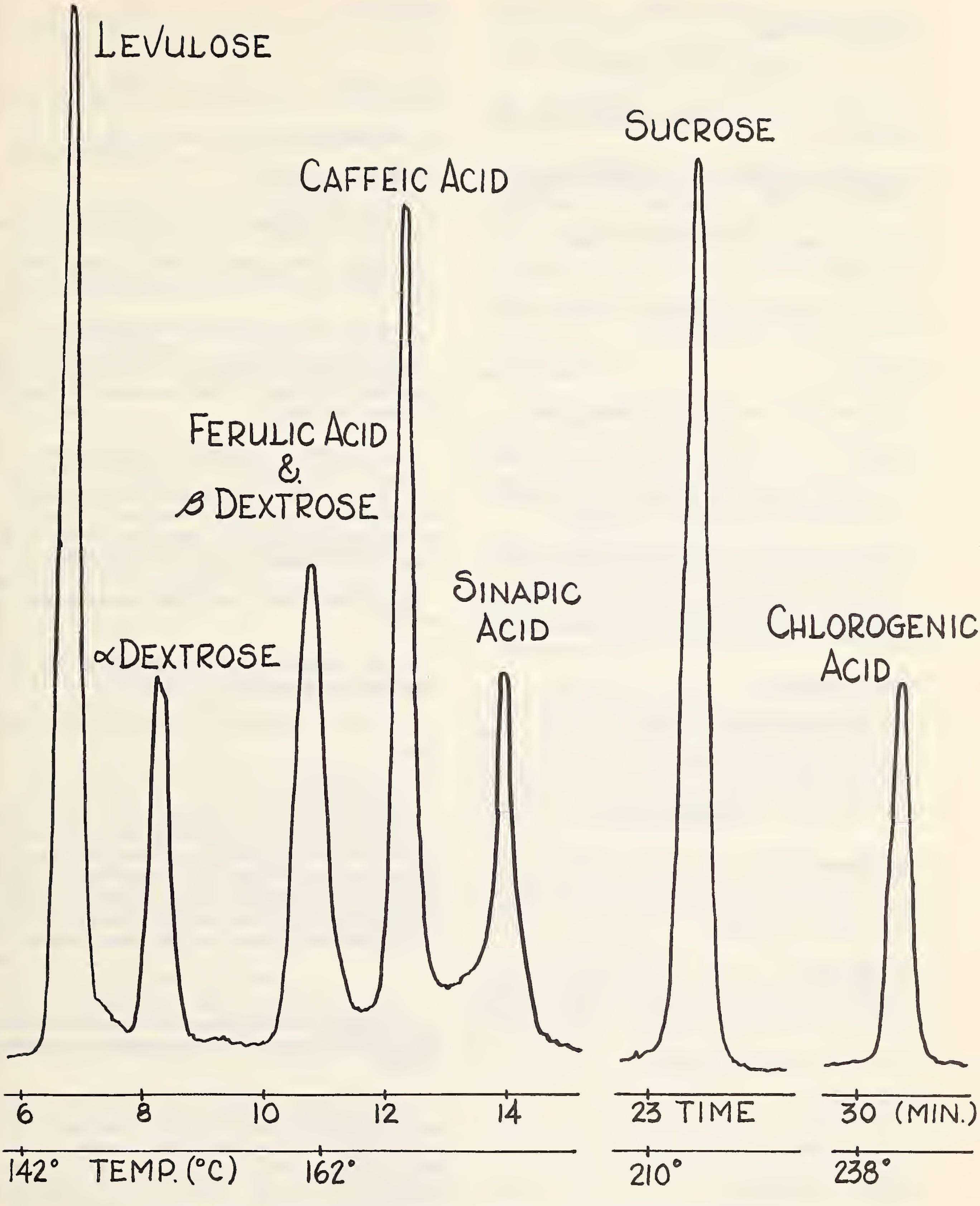

Figure 12. — Separation of colorants and sugars in JXR column programmed at 118° to 240° C. at 4° min.

Phenyl Beta-D-glucoside — Nutritional Biochemicals Corp, Cleveland, Ohio

Trizil-Z — Pierce Chemical Co., Rockford, Ill.

Chlorogenic Acid — Aldrich Chemical Co., Inc, Milwaukee, Wis.

3,4-Dihydroxy-Cinnamic Acid — Aldrich Chemical Co., Inc., Milwaukee, Wis.

4-Hydroxy-Cinnamic Acid — Aldrich Chemical Co., Inc., Milwaukee, Wis.

3,5-Dimethoxy-4-Hydroxy-Cinnamic Acid — Aldrich Chemical Co., Inc., Milwaukee, Wis.

Instrument

F & M Model 810 Analytical Gas Chromatograph

Column

1) 6-ft. Coiled stainless steel, packed with 5% SE-52 on 80/100 mesh Chromosorb-G (AW-DMCS).

2) 1/8″ N 18″ column, packed with 3% JXR coated on 80/100 mesh Chromosorb-W (AW-DMCS).

Both were obtained from Applied Science Laboratories, Inc, State College, Pa.

Operating Conditions

Injection port temperature — 300°C.

Detector temperature — 300°C.

Oven temperature — programed as below.

Sugar Determination

SE-52 — 170° to 300°C. at 1°/min. until the elution of β-dextrose, then 2°/min.

Sugar Colorants

SE-52 — 170° to 300°C. at 2°/min.

JXR — 118° to 240°C. at 4°/min.

Gas Flow Rates

Carrier gas (Helium) — 50 ml./min.

Hydrogen — 60 ml./min.

Air — 300 ml./min.

Sample Size

5 μl.

Attenuation

As determined by trial run.

Procedure For Silylation

A. Sugar determination

1. Sugar solutions were weighed accurately (about 150 to 200 mg.) in a 50 ml. volumetric flask.

2. 10 to 20 ml. pyridine was then added.

3. Sugar-pyridine solutions were then placed in a water bath at 65° to 70°C. with occasional shaking for 20 minutes and cooled.

4. It was then diluted to 50 ml. with pyridine.

5. 5 ml. of the solution was pipetted into a 50 ml. ground glass joint Erlenmeyer flask with 1 ml. of a 3 mg./ml. pyridine solution of sorbitol and 1 ml. of a 4 mg./ml. pyridine solution of phenyl B-glucoside.

6. To the mixture 5 ml. HMDS was added and 0.5 ml. TFA.

7. The reaction was allowed to subside, and the flask then shaken vigorously.

8. It was then refluxed for 15 minutes over a hot plate.

B. Sugar Colorants

10-20 mg. of each of the colorants, levulose, dextrose, sucrose, and internal standards were weighed into a 25 ml. Erlenmeyer flask and 10 ml. pyridine added to dissolve the mixture. The solution was treated with 10 ml. hexamethyldisilazane and either 0.5 ml. trimethylchlorosilane or 1.0 ml. trifluoroacetic acid.

DISCUSSION

L. MAHONEY: Would you please comment on the practical use of gas-liquid chromatography for refinery control.

V. S. VELASCO: Gas-liquid chromatography could be very useful in quality control in determining the dextrose-levulose breakdown. For example, if the dextrose-levulose ratio were high, this would indicate destruction in the levulose. Also, gas-liquid chromatography could be used to determine percent corn syrup in a blend of sugar.

S. B. SMITH: Are these columns standard accessories?

V. S. VELASCO: The columns are standard and can be purchased from any supply house.

G. A. HAGENEY: What are the lowest levels of dextrose and levulose that you can detect accurately?

V. S. VELASCO: We have tried about 9 percent invert and we still get the same accuracy.

G. A. HAGENEY: Did you go down to anything lower than 9 percent?

V. S. VELASCO: No, we did not. In the future, we'll be trying different concentrations, and will vary the percent solids of the sugar mixture. We went as low as about 9 percent invert so far, and as high as about 80 percent.

G. A. HAGENEY: How would you expect results to be, if you went down to something like 1 percent or one tenth of one percent?

J. F. DOWLING: About five years ago we ran raw sugars, and we were able to get an estimate of the D/L ratio, but we did not carry this work any further until we were able to determine the precision of our measuring technique.

G. A. HAGENEY: For the separation of the dextrose, the levulose and the sucrose, you were using 20, 20 and 20 percent; what else did you have in there, since that doesn't add up to 100?

V. S. VELASCO: This is liquid sugar, not solid. The rest was water. We did most of this work on the same percent solids. We did some work at 20 and 50 percent, but the results were the same.

K. R. HANSON: When you were using your mixtures with mono- and disaccharides, you found sucrose at about 55 minutes. Did you ever let your chromatograph run out to 2 and 3 hours, and if so, did you find anything?

V. S. VELASCO: We ran it only for 1 hour. We were approaching the temperature limit and runs of 2 hours or 3 hours would have destroyed the column.

J. F. DOWLING: When you run a sample like this, if you don't get the sucrose out after 1 hour, it is probably not going to come out that day.

W. W. BINKLEY: Did you try a planimeter to measure the area under the curve?

V. S. VELASCO: The peakometer which we mentioned is a planimeter, and we found very poor reproducibility so we decided to use the ruler with the height × width at half-height method.

W. W. BINKLEY: Did you try cut and weigh?

V. S. VELASCO: No, we didn't try that.

W. W. BINKLEY: Did you run chromatographs on final molasses?

V. S. VELASCO: We have done analysis on final molasses, and we didn't have any trouble in derivatizing the sample. It came out with the same separation, but we did not investigate the quantitation of the sugars — whether that was reproducible or not.

W. L. REED: You seem to have very good precision on the various tests you've illustrated. Do you have any difficulty with anything interfering, other than, apparently, the ferulic acid. If you were able to handle final molasses, I assume you could handle almost anything.

V. S. VELASCO: Yes, that is an advantage of this method. If you are interested in sugar colorants, you might not be able to see the sugar colorants in the whole sugar because they are present in very minute quantities. There is a need for separation as well as for concentration of the sugar colorants, before you could employ a GLC method of analysis.

W. L. REED: At what stage above final molasses would you have to apply separation — could you do it on almost any mixture of the appropriate purity in a refinery?

V. L. VELASCO: I'm sure you could measure sugars at any stage in the refinery, but to determine colorants, separation and concentration will be needed even in molasses.

USE OF CHLORIDE ELECTRODES IN REFINERY CONTROL

by

P. Pommez and S. Stachenko
Canada and Dominion Sugar Co. Ltd.
Montreal, Quebec, Canada
(Presented by P. Pommez)

ABSTRACT

Chloride was found to be most suitable for monitoring the affination process. Although chloride can be determined accurately by a potentiometric titration, specific chloride ion electrodes are attractive because of their speed and possibility of on-line use. Experimental work with two types of electrodes showed that best results were obtained with a solid state model. Response of the electrode is critically dependent on the temperature, Brix, and flow conditions of the liquor around the electrodes.

INTRODUCTION

We propose first to review the reasons which led us to suggest the use of chloride determinations as a criterion for the control of the affination process, and then to describe procedures which are recommended for the chloride analysis of refinery sugar products.

AFFINATION PROCESS

It should be clear that, before one can decide which is the best approach to evaluate the performance of the affination station, the objectives which are to be achieved by this process must be well defined. In our view, the idealized affination process is the one which would eliminate the film of residual mother syrup remaining on the surface of the raw sugar crystals without substantially affecting or dissolving the crystals themselves.

If we accept the fact that the removal of only this outer film is the measure of true affination efficiency, we imply that the affined sugar will still contain all the impurities that are not present in the outer film. We realize that this concept is incompatible with most standard operating procedures which tend to impose fixed maximum impurity limits on the washed raw sugar, say .12 percent invert and/or .12 percent ash.

However, we feel that increasing the wash to satisfy a quality constraint can only be a short-term solution which will eventually catch up with one, since by definition the first crop remelt sugar must be worse than washed raw (assuming equivalent wash percent solids). The white sugar processing path is presumably designed for some average quality standards and one should be prepared to allow variations around set points instead of upsetting the total solids flow in the recovery plant.

More data of course would be useful to verify exactly the cost impact in "possible lower color removal efficiency of char", if ash content in washed sugar liquor is high, as against higher cost in increased remelt pan boilings, and colour pickup throughout remelt system. However, it would seem to us offhand that we try to look too closely at the immediate effects visible within the white sugar system and lose track of the longer term, not so easily verifiable, results from the recovery end. Whatever we chase out of the white, must come back sometime.

Having then defined our "modus operandi," we must now determine how well the film is being removed from the crystals, and hence how much wash water to apply. To verify the efficiency of the affination process, more than 100 average samples of raw sugar cargoes were submitted to a standard affination which was designed to give a washed raw sugar with a minimum dissolution of sugar crystals. The procedure used for standard affination is described in Appendix A.

Analysis of various constituents before and after affination gave an indication of the effectiveness of the standard affination in removing given impurities from the original raw sugar. A typical set of results is enclosed in Appendix B. These results were also analyzed statistically and the variation in percent elimination of different inputs is as follows:

	Percent removal in affination	
	Mean	Standard deviation
Chloride	89.59	3.89
Ash	76.17	7.93
Invert	73.80	11.62
Color	75.85	7.53
Calcium carbonate	71.65	8.16
Potassium	84.41	6.02
Sodium	80.40	5.42
Starch	47.47	20.13
Gums	65.21	27.97

From these results, it was clear that removal was greatest for chloride, and furthermore, that the variation in removal for raws of different origin was the least for chloride. The conclusion was that under ideal affination conditions, one should expect consistent removal of about 90 percent of chloride present in the raw sugar. Chloride control is thus used as a measure of "film."

It should be noted that it is not too surprising to find chloride concentrated in the outer film. If one considers the crystallization process in the production of raw sugar, the repartition of impurities in and around the sugar crystal will depend either on the affinity of impurities for the sugar crystal or on the respective solubilities of the non-sucrose components.

In the case of chloride, possible cocrystallization with sucrose is most unlikely, whereas components such as dextran, coloring matter, etc. are known to be included in the sugar crystal. The exact mechanism of the inclusion is not too well known, but suffice it to say that chloride is an unlikely candidate for this inclusion.

Another factor that relates to the ease of removal of chloride is its solubility. We have studied the removal of various ions throughout the affination process. From these results, a pattern of ionic removal emerges as shown below:

	Average of 26 weeks		
Anions	Raw µeq/g. solids	Washed raw sugar µeq/g. solids	Percent removal
Cl	25.0	3.1	87.5
Organic anions	24.1	4.9	78.4
SO_4	16.8	6.0	65.0
PO_4	4.1	1.3	68.2
Cations			
K + Na	20.3	2.8	86.0
Ca + Mg	25.8	9.5	59.0

Monovalent ions are obviously better removed than polyvalent ions. We have also followed more closely the removal of potassium and sodium individually and found that in cane sugar refinery products, of the two ions, only potassium is significant, since the ratio of potassium/sodium is about 20.

Flame photometry was used for the determination of these ions, and we found that throughout affination process, the ratio of potassium/sodium remained constant. We have another reason to be particularly concerned about removing the monovalent ions in affination. It was shown in an ionic constituent survey that the chlorides can only be removed in the affination process, whereas polyvalent ions can be removed during further processing stages, such as carbonatation and charring.

Another consideration of added significance in the choice of chloride in this control was analytical precision for the determination of the various impurities which can be measured in the raw and washed raw sugar. Statistical data given in Appendix C show that the method of determination for chloride is statistically more precise than any other method.

METHOD OF CONTROL

At first we thought that if we could simply sample raw sugar frequently, or continuously, determine chloride in it, and correct wash for given changes, we would get optimal control. However, this is not correct for the simple reason that what is really going to determine the amount of residual chloride in the washed raw sugar is the adequate removal of both the mingling syrup and the raw sugar film. If the chloride in the raw sugar changes, there will be no immediate effect until the mingling syrup reaches a new equilibrium position in composition, assuming ideal conditions for washing efficiency.

The control of wash by direct relationship to quality of raw input would tend to overreact. The most valid sample point for chloride control should be the raw magma, but this is rather difficult to sample. One must point out, however, that all other conventional methods of control (invert, ash) are susceptible to the same constraints, and in fact, are even more influenced by quality of raw.

The compromise solution would be simply to allow for a standard removal setting (say 90 percent of input), and simply keep checking chloride in washed raw sugar as a function of chloride in raw magma. We think that under these conditions drift would be slow and that chloride level should be allowed to vary within a reasonable range before making adjustments.

PRESENT METHOD OF CONTROL OF AFFINATION

There are two phases of affination control:

1) Determination of the required wash.

2) Control of wash duration to maintain the required wash.

The two phases using the computer for control are described below:

Determination of required wash: The criterion used is that an increment of the wash quantity should produce a minimal decrease in the washed raw sugar chloride level. As on-line chloride measurement has not yet been achieved, this point must be determined from laboratory measurements. The procedure is:

(a) Call program R — This causes the total duration of wash on one affination machine to vary progressively during succeeding cycles (Machine No. 2 is used because this is most easily accessible for sampling). Typical durations might be 8, 12, 16, 20 and 24 seconds over the next five machine cycles. The wash duration then reverts to the current value.

(b) Collect samples of the washed raw sugar corresponding to each machine cycle and determine the chloride level.

(c) Punch a tape containing the wash durations and chloride levels.

(d) Call program T to check that the tape contains no format errors.

(e) Call program W. This first performs a regression analysis to derive an equation of the form:

$$C = A + B/w$$

where:
C = chloride level
w = total wash duration
A & B = coefficients to be determined.

(The correlation coefficient for the regression is calculated and the results rejected if the value is less than .9. A "check data" message is printed).

If the results are acceptable, the resulting equation is printed. The optimal wash is that at which the chloride-vs-wash curve has a specified slope. The optimal wash and expected chloride level is printed as part of a table containing the expected chloride levels at washes above and below optimal.

(f) The newly calculated wash goes into immediate effect.

Control of wash: No further intervention is required to maintain precise control of affination wash. The control logic is as follows. It is assumed that the wash water Brix was effectively zero during the regression sampling. The calculated duration and the current flow rate per second are used to determine the wash water volume per machine cycle.

If the Brix of the wash water changes (because of the addition of char lights), the wash duration is adjusted to maintain a constant quantity of water per cycle (i.e. the total wash volume is increased with Brix). Also, the flow rate per second is continually monitored and used to adjust the total wash duration. This compensates for changes in the wash water viscosity or the flow characteristics of the valve and supply line.

The computer gives simple, yet precise control of affination wash. The absence of an on-line chloride measuring device makes the determination of the optimal wash a little cumbersome. However, the aim is to associate a particular volume of wash water per cycle with each type of raw. The wash volume could then be set to correspond to the origin of the raw and the measuring procedure used only for occasional checking.

CHLORIDE DETERMINATION

Having shown the reliability of the chloride value as a measurement of the affination efficiency, a fast and reliable chloride determination method remained to be found. The most precise results were given by the silver nitrate potentiometric titration described in Appendix D.

To test reliability of this method, a series of chloride determinations was carried out on samples from different origins, each sample being analyzed ten times. The results for the chloride level in washed raw sugar are as follows:

Cl percent arithmetic mean : .0060
Standard deviation : .00013
95 percent confidence limits : ±.00003

Thus the potentiometric method would be an excellent control instrument; the only objection is that accuracy of the method would not compensate for the lag between sampling and analysis. The ideal of course would be to measure the chloride on line, using an instrument sensitive enough to detect low changes in concentration, and that with a short response time. For this purpose we investigated recently marketed ion-selective electrodes.

The electrode tested was an Orion Solid-State Membrane Electrode, Model 94-17. An Orion Combination Chloride Electrode was tested first, but it was discarded after it had shown several deficiencies.

Principle of ion-selective electrodes[1] An ion selective electrode consists of an insulating glass or plastic tube sealed across one end by a membrane as shown in fig. 1. The tube usually contains a solution of the ion to be measured and an internal reference

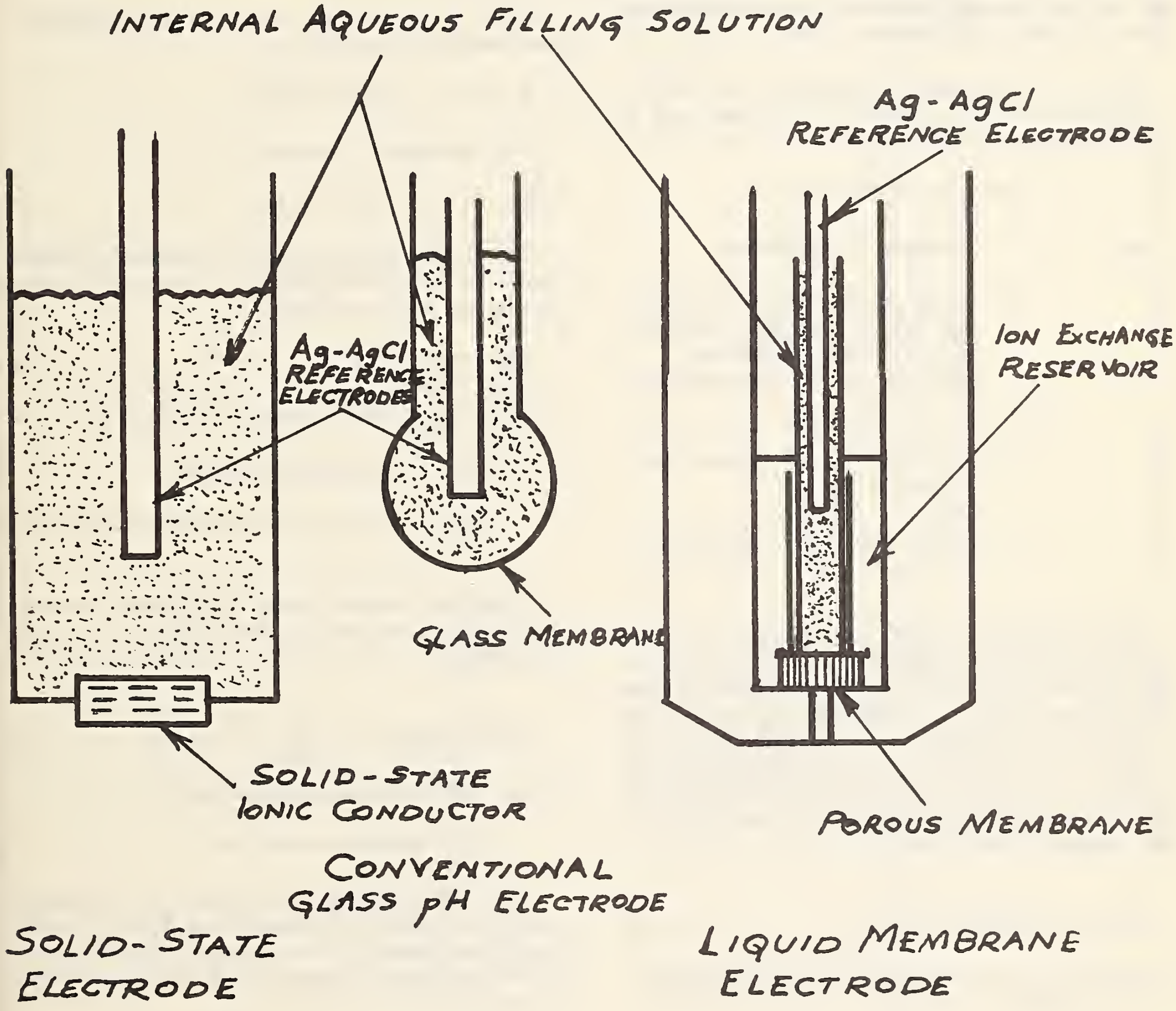
INTERNAL AQUEOUS FILLING SOLUTION
Ag-AgCl REFERENCE ELECTRODE
Ag-AgCl REFERENCE ELECTRODES
ION EXCHANGE RESERVOIR
GLASS MEMBRANE
SOLID-STATE IONIC CONDUCTOR
POROUS MEMBRANE
CONVENTIONAL GLASS pH ELECTRODE
SOLID-STATE ELECTRODE
LIQUID MEMBRANE ELECTRODE

Figure 1. — Ion-selective electrode.

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[1] Weber, Stephen G. 1970. Amer. Lab. July.

electrode (calomel or silver-silver chloride). A voltmeter or pH meter with expanded millivolt scale is used to measure the potential developed between the ion-selective electrode and an external reference electrode when the pair is immersed in a solution.

The selectivity of the system depends on the characteristics of the membrane. This membrane functions as a barrier which allows only the desired ion to pass—by diffusion—between the sample solution and the internal filling solution. Diffusion results from a difference in activity between the two solutions. When the activity of the ion in the sample solution exceeds that in internal solution, there is a net diffusion of ions into the electrode. The transport of ions continues until a state of equilibrium is reached, at which point the electrical potential developed across the membrane prevents a further net diffusion of ions.

The value of the membrane potential varies with the concentration of the ion in the sample, and is determined by the Nernst equation.

$$E = E_o + 2.3\ (RT/nF)\ \log A$$

where:

E = potential at equilibrium

E_o = the portion of the total potential due to the choice of internal and external reference electrode and internal solutions.

RT/F = the Nernst factor.

n = the magnitude and sign of the charge on the ion

A = activity of the ion in the sample solution.

In the chloride electrode the membrane is a silver chloride crystal. This membrane is an ionic conductor for silver ions and the internal filling solution contains a fixed level of silver ion. Although the silver is the mobile ion, the non-silver ion, e.g. chloride, can be measured since its activity in the sample affects the solubility of the silver salt, and it is the difference in silver ion activity across the crystalline membrane that the electrode potential reflects.

$$E = E_o + 2.3\ RT/F \log A_{Ag^+} \qquad (1)$$

where: A_{Ag^+} = the silver ion activity in the sample solution.

The silver ion activity can be calculated from the solubility product (K_{sp}) of silver chloride.

$$A_{Ag^+} = \frac{K_{sp}}{A_{Cl^-}} \qquad (2)$$

When this value for A_{Ag^+} is substituted in equation (1), the relationship between the total electrode potential and chloride ion activity in the sample solution is:

$$E = E_o + 2.3\ RT/F \log K_{sp} - 2.3\ RT/F \log A_{Cl^-}. \qquad (3)$$

Since K_{sp} is constant at any given temperature, a new constant can be defined:

$$E_1 = E_o + 2.3\ RT/F \log K_{sp}.$$

Thus equation (3) becomes:-

$$E = E_1 - 2.3\ RT/F \log A_{Cl^-} \qquad (4)$$

Activity and concentration: The following equation shows the relationship between the sample chloride activity and the concentration:

$$A_{Cl^-} = \gamma_{Cl^-} \times C_{Cl^-} \qquad (5)$$

where:– A_{Cl^-} = the sample chloride ion activity.

γ_{Cl^-} = the activity coefficient.

C_{Cl^-} = the sample chloride ion concentration.

If the approximate sample composition is known, the total ionic strength can be estimated by using the equation:

$$\text{Ionic Strength} = 1/2 \sum (Z_i^2 \times C_i) \qquad (6)$$

where: C_i = the concentration of each ion.

Z_i = the charge on this ion.

From the total ionic strength value, it is possible to obtain the activity coefficient using figure 2, where total ionic strength in moles/litre is plotted versus activity coefficient calculated from the Debye-Huckel Theory.[2]

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[2] Kielland, J. 1937. Individual activity coefficients of ions in aqueous solutions. Jour. Amer. Chem. Soc. 59: 1675-1678.

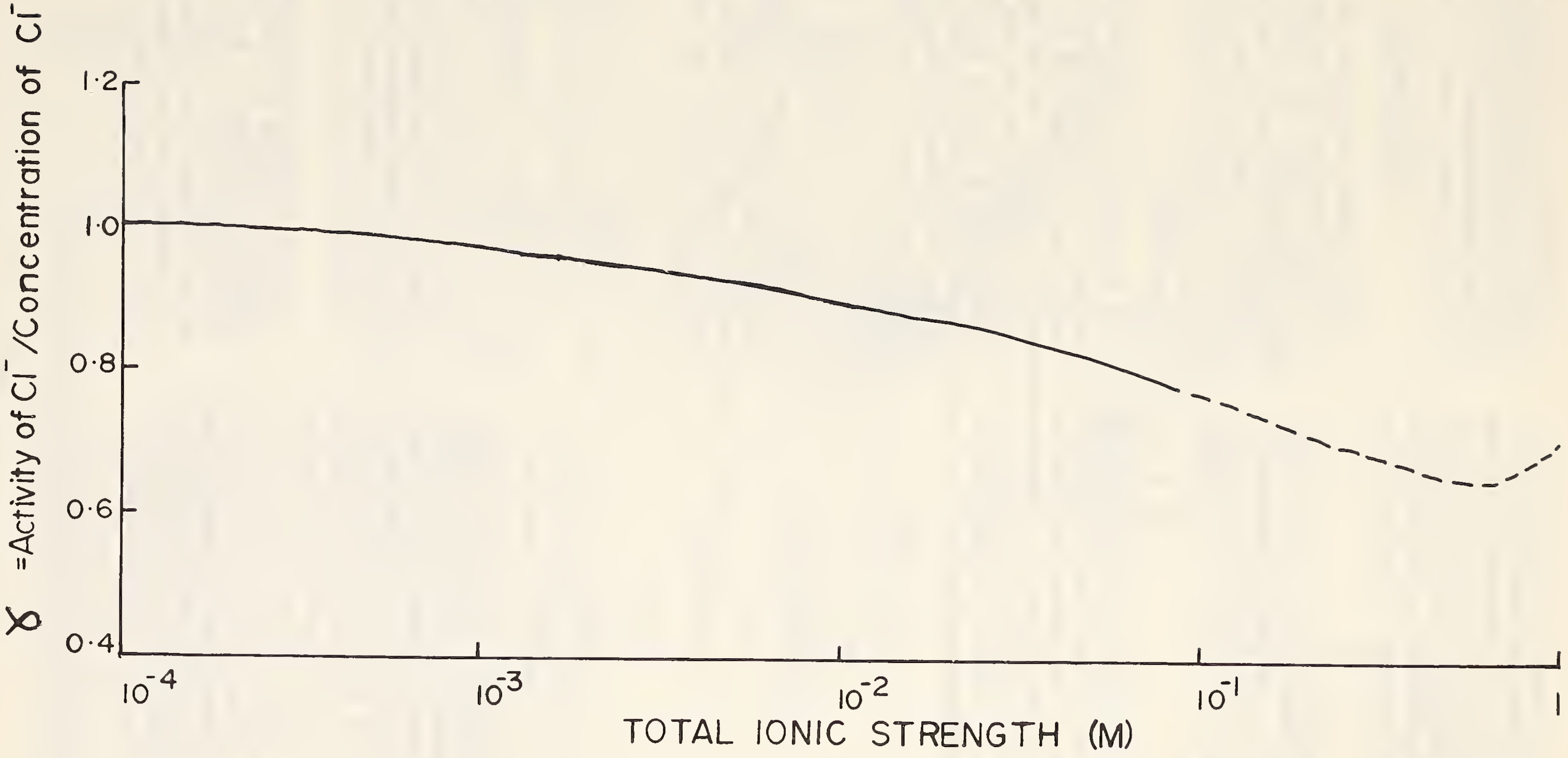

Figure 2. — Variation of chloride activity with total ionic strength of the solution.

In all our lab experiments, sucrose solutions were made with deionized water (ionic strength $<1.1 \times 10^{-4}$ moles/litre as measured by conductivity) and sugar with a .001 percent ash content. At this point, it was estimated that the total ionic strength of the prepared pure sucrose solution would be essentially due to the sodium and chloride ions added for the purpose of the test.

As the electrode was tested for a chloride concentration ranging from 0.5×10^{-3} to 10.0×10^{-3} M, total ionic strength was estimated to range within the same values giving an activity coefficient between 0.98 and 0.91. The chloride concentration is expressed in moles/litre of water.

Interference: The electrode will malfunction if ions which form very insoluble salts of silver are present at sufficiently high levels to form a layer of the salt on the membrane surface. The following table gives the maximum allowable concentration of the more common interfering ions as given by the manufacturer and expressed as the ratio of the interfering ion concentration to the chloride concentration.

Interference	Maximum ratio
OH^-	80
Br^-	3×10^{-3}
I^-	5×10^{-7}
S^-	Must be absent
CN^-	2×10^{-7}
NH_3	0.12[3]
$S_2O_3^{=}$	0.01[3]

Reference electrode. The choice of a suitable external reference electrode is very important, because of the junction potentials between the internal filling solution of the reference electrode and the sample solution. Most laboratory pH measurements are made to an accuracy of 0.1 pH unit which corresponds to approximately 6 mV in electrode potential. When one considers the accuracy required in the potential measurement, one tries to obtain an accuracy of 1 to 2 percent in the activity of the ion being determined. This requires an accuracy of 0.1 to 0.2 mV in the electrode potential measurement. The factors affecting the liquid junction potential involve essentially the mechanical construction of the junction, and the composition of the liquid function filling solution.

Characteristics of our working solutions have induced us to use an Orion double junction reference electrode Model 90-02. With the voltmeter we used, we could only claim an accuracy of 1 mV, corresponding to an error of about 3 percent on the chloride value.

EXPERIMENTAL

Measurements were made at thermostatically controlled temperature, and homogeneity was ensured by magnetic stirring. The chloride and reference electrode were connected to a Radiometer titrator type TTT1 set to −300 + 300 mV. The output of the titrator was connected to a Bausch & Lomb VOM-5 recorder. Care was taken to immerse the electrodes at a constant depth.

At the same time, chloride level in the sample under examination was determined by the potentiometric method and the values obtained were used for calibration. In order to test the effect of flow, dynamic conditions were simulated in the lab set-up, shown in figure 3. Flow rate was controlled by using a Varistaltic pump. Turbulence taking place around the electrode was observed by addition of methylene blue in the sample vessel and visual observations of the streams.

RESULTS

Response of the electrode in deionized water. — The following table gives mV values against different chloride concentrations in deionized water at 25°C in static condition, i.e. the sample just stirred magnetically in a beaker.

Cl^- mN	mV
0.64	170
1.36	153
2.73	136
5.30	120
7.88	108

The Nernst factor calculated from the calibration curve gives a value of 59 mV as compared to the theoretical value 59.16 mV at 25°C. Figure 4 shows the calibration curve.

Response of the electrode in flow conditions. — Effect on flow was tested using the lab set-up shown in figure 3. It was found that the electrode potential depends critically on the flow rate, and this effect has to be considered before installing the electrode on line. Once a steady reading had been reached, good correspondence was found between

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[3] Represents species which form extremely stable complexes with silver ion.

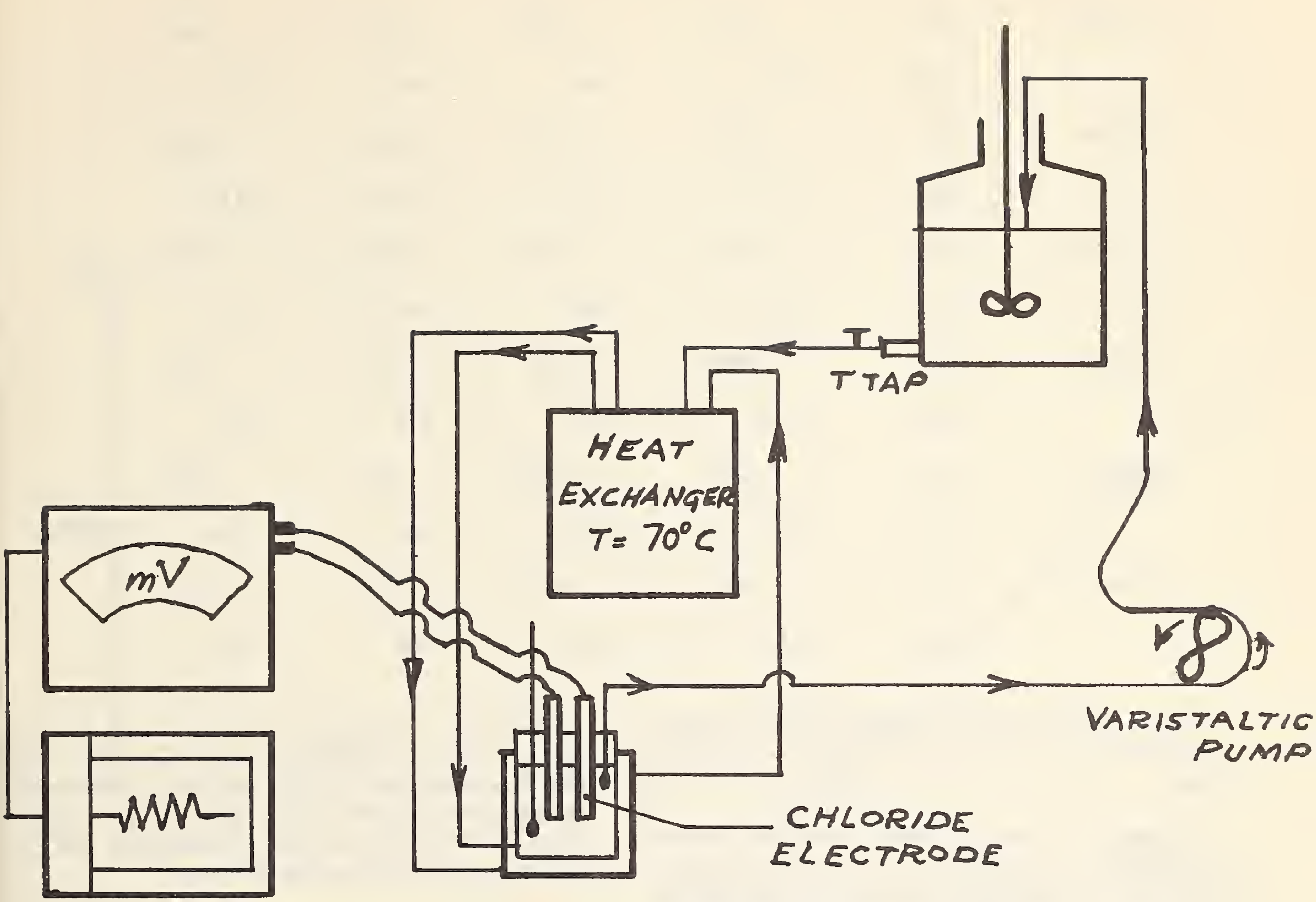

Figure 3. — Chloride electrode study.

figures from static and dynamic conditions, the average deviation from the static values being ± 1.5 mV.

Electrode response time. — To measure the response time of the electrode to a change in the chloride concentration, known chloride amounts were added to the sample vessel (fig. 3) with the tap T closed and the reaction tank full of the original liquor. A stopwatch was started when T was opened and the pump started. The stopwatch was stopped when a steady value was obtained on the recorder chart.

The following table gives results:

Cl^- mN	mV	Response time (min)
0.97	180	2.30
1.94	162	4.00
3.87	144	3.20
5.81	135	1.40
7.75	128	4.40
9.69	122	4.40

The average response time was 3.30 minutes in a 60° Brix solution at 70°C. A large part of this time was required for homogenization of the solution since the electrode, when placed in the same solution in a beaker at 25°C, gave a steady result after 1 to 2 minutes. So from a practical point of view response time of the electrode would be negligible compared to the lag involved with any change of chloride concentration in the plant.

Response of the electrode in sucrose solution. — To evaluate how the electrode response was affected by the presence of sucrose, a series of tests was performed on sucrose solutions ranging from 0° to 60° Brix, in flow conditions, at 25°C, for different chloride concentrations. Results are grouped as follows:

10° Brix	Cl^-	.467	1.047	2.09	5.92
	mV	183	163	148	123
20° Brix	Cl^-	.508	1.143	2.20	6.39
	mV	182	165	149	121
30° Brix	Cl^-	.557	1.265	2.45	7.00
	mV	180	162	147	118
40° Brix	Cl^-	.632	1.428	2.74	7.84
	mV	177	158	142	114
50° Brix	Cl^-	.697	1.672	3.12	8.99
	mV	174	152	139	110
60° Brix	Cl^-	.835	2.075	3.78	10.74
	mV	165	148	133	104

Figure 5 shows the curve obtained by plotting these points compared to the calibration curve in deionized water.

Remarks: — It must be remembered that chloride concentration is expressed in moles/litre of water. However, we do not know how the volume of water at the disposal of the chloride ion can be affected by the presence of sucrose molecules.

Assuming no effect of sucrose, if we add the same weight of chloride to the same volume (at 25°C) of sucrose solutions at different concentrations, mV readings should decrease (in the same way that the volume of water decreases and chloride concentration increases) as the Brix increases.

In fact, we have observed an abnormally low mV value between 10° and 20° Brix, suggesting the possibility of some water molecules being picked up by the sucrose molecule. This could be related to many thoughts concerning existence of highly hydrated sucrose molecules in the low molar concentration range.

Effect of temperature. — Influence of temperature was examined. Figure 6 shows how the electrode response varies in a 60° Brix solution, under flow conditions, with respect to the temperature at two different concentrations.

Electrode response in raw washed sugar liquor. — Using the calibration curve made with a 60° Brix sucrose solution at 70°C, we tried to calculate the chloride level in melter liquor from the mV reading. Chloride obtained was always higher than chloride determined by potentiometric technique.

Then we started to study the electrode behavior in melter liquor when known amounts of chloride were added. Figure 7 shows values corresponding to the different raw washed sugar liquors compared with pure sucrose calibration curve. Comparing the ionic composition of affined sugars and pure sucrose, it appeared that the difference observed in the response could be due to the difference in total ionic strength between reference and sample solutions. As a matter of fact, considering ionic composition of washed raw sugar[4],we have:

Ion	Micro equivalents /gram solids
$Ca^{++} + Mg^{++}$	14.2
$K^+ + Na^+$	9.5
$SO_4{}^=$	9.1
Cl^-	3.8
$PO_4{}^{3-}$	1.9

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[4] Stachenko, S. 1961. Proc. 7th Tech. Sess. Bone Char. 63-66.

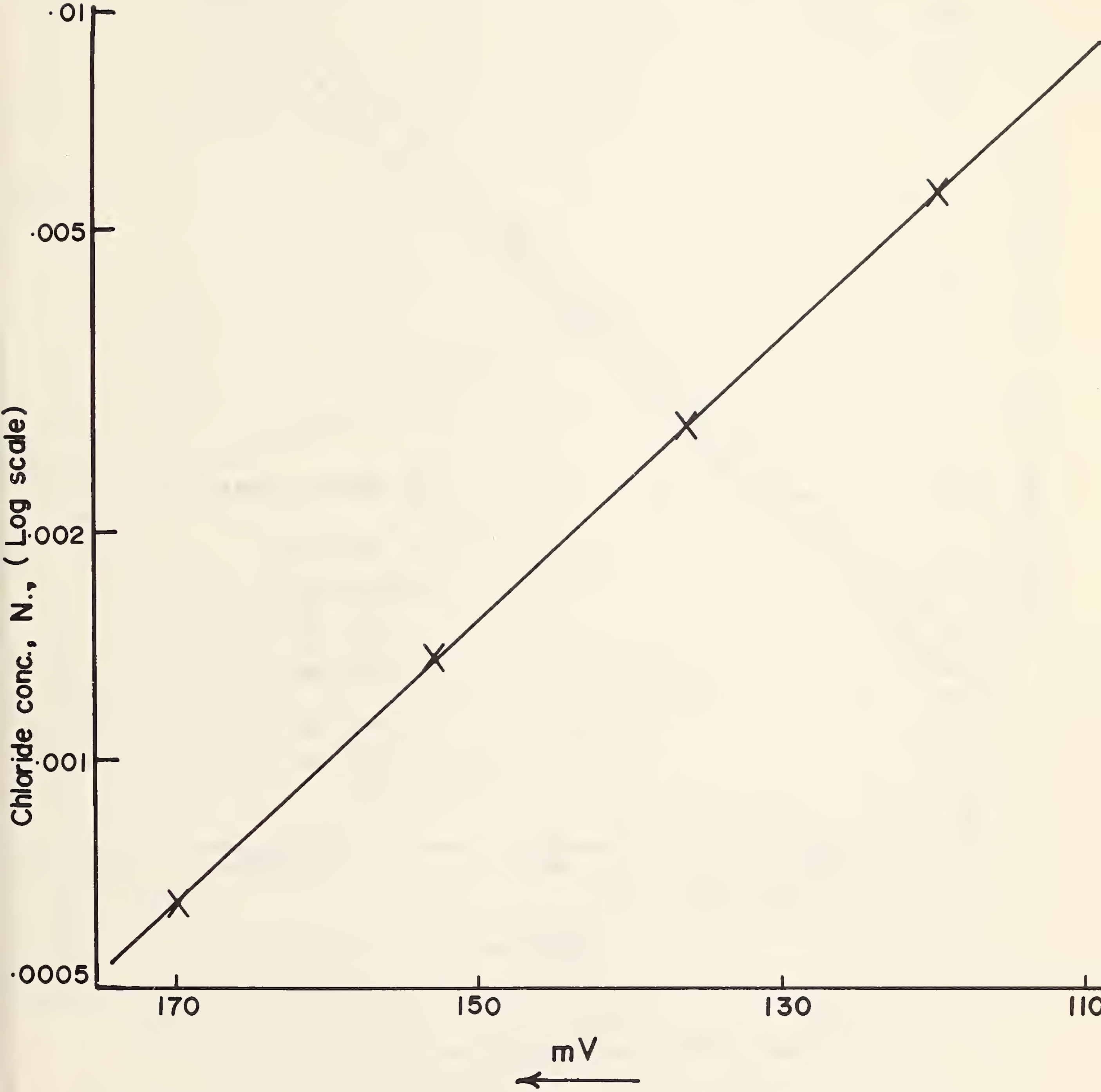

Figure 4. — Chloride concentration vs millivolts in deionized water at 25° C.

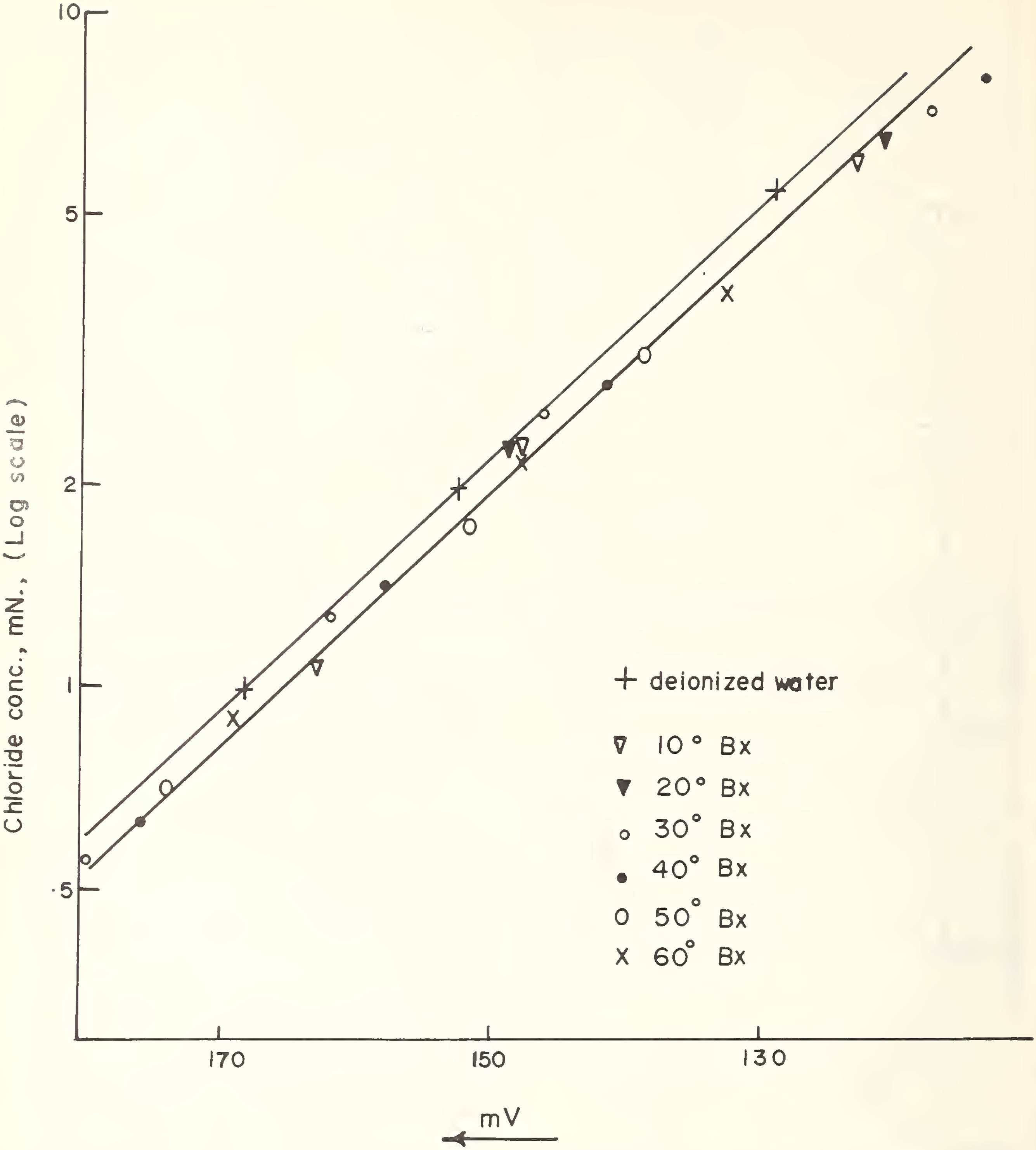

Figure 5. — Chloride electrode in sugar solutions at 25° C.

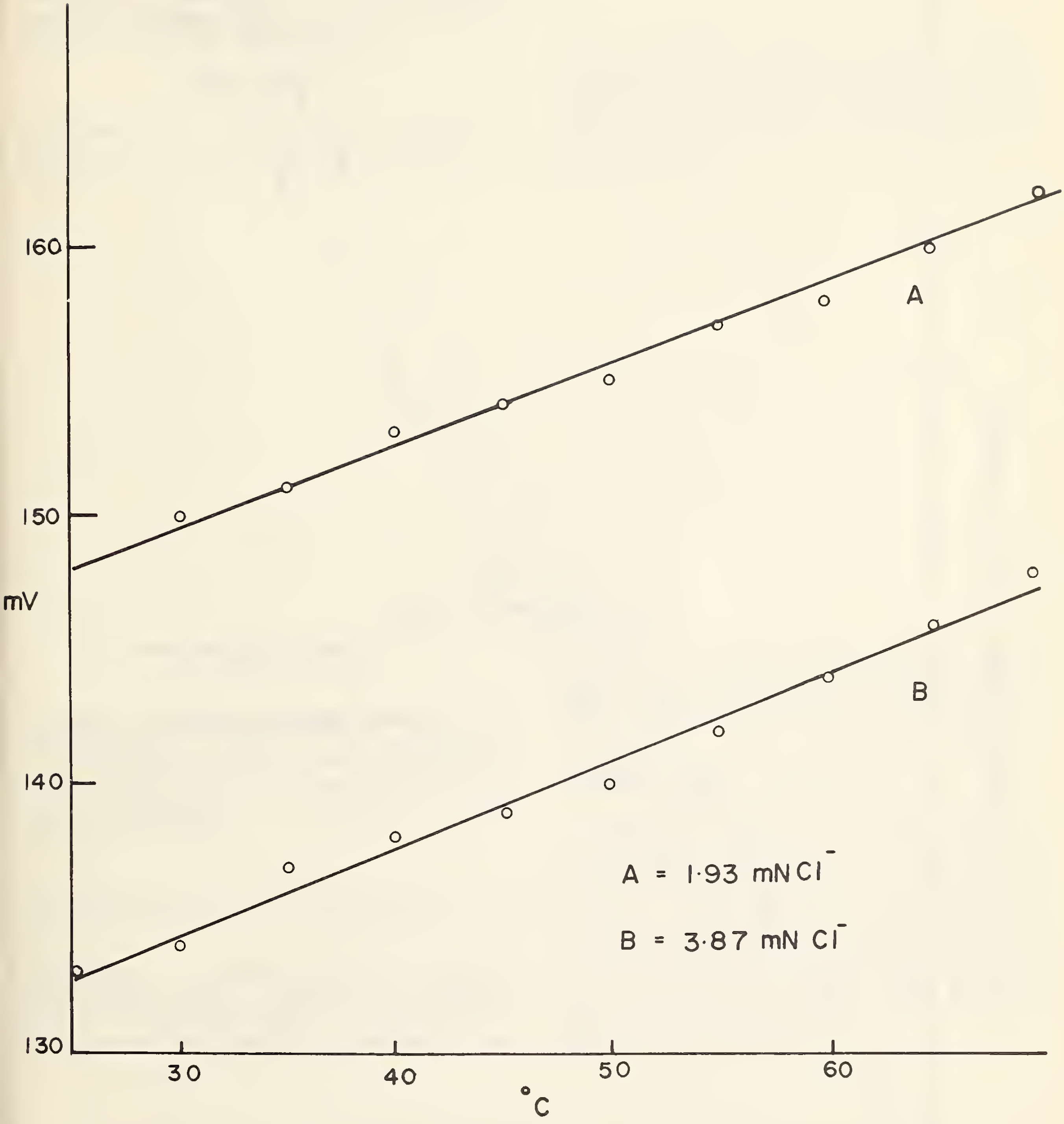

Figure 6. — Effect of temperature in 60° Brix sucrose.

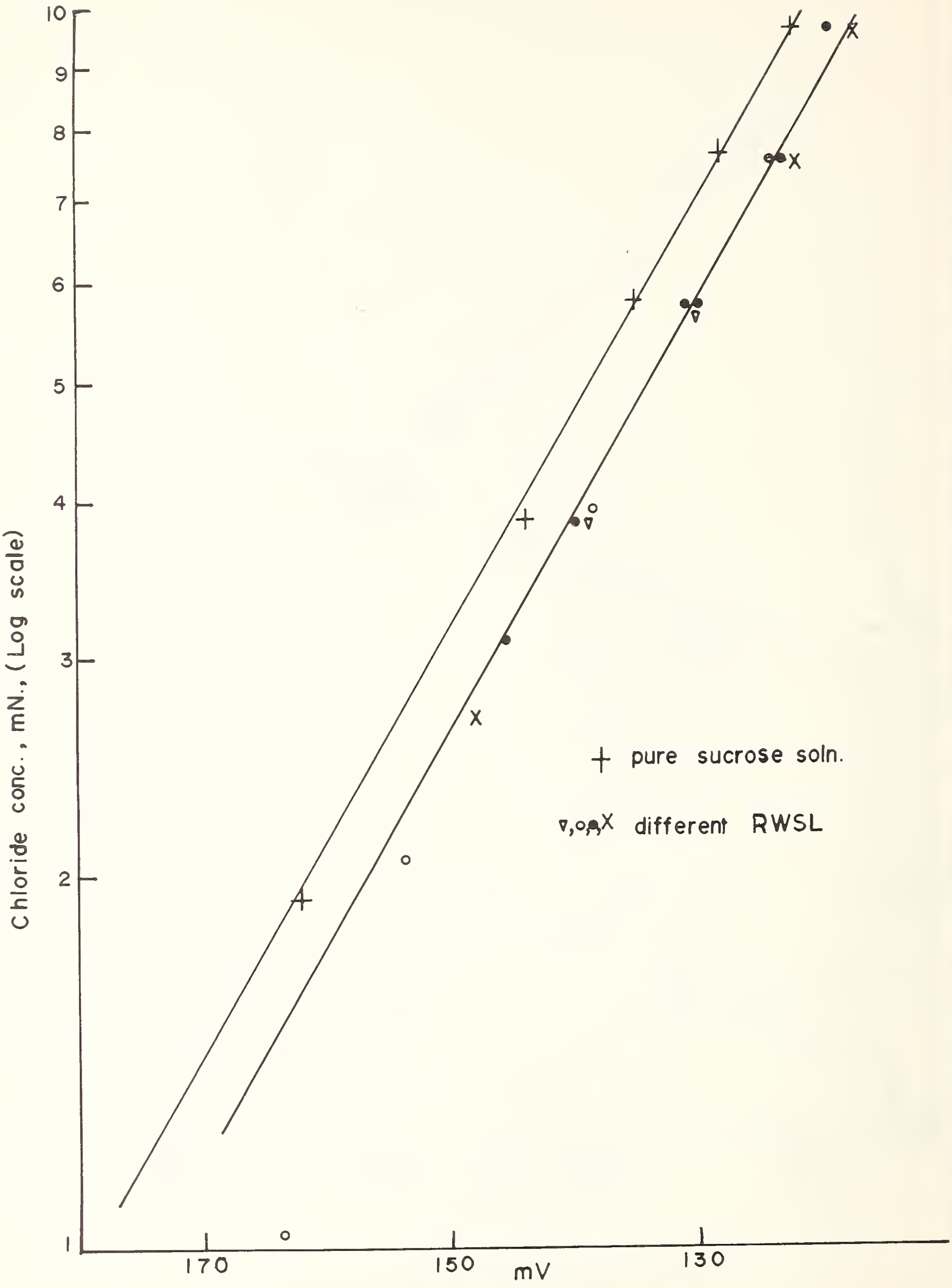

Figure 7. — Chloride electrode response in 60° Brix sugar liquors at 70° C.

The total ionic strength calculated by using equation 6 is found to be 7 × 10^{-2} moles/litre, corresponding to a chloride activity coefficient $\gamma = 0.80$. Effect on ionic composition is also pointed out in figure 7, where the point deviating most from the RWSL curve corresponds to a beet raw sugar of which the ionic composition is different from the cane raw ash composition. This effect is less visible after addition of NaCl to act as an ionic strength adjuster.

CONCLUSION

We have shown the validity of the chloride measurement as a control method for measurement of affination efficiency. The most accurate chloride determination method is to use potentiometric techniques, but this method has the disadvantage of a more or less long delay between sampling and measurement.

On the other hand, the on-line chloride determination by use of the ion-selective electrode is very attractive. Further refinements involving differential techniques will be studied under plant operating conditions.

APPENDIX A

Canada & Dominion Sugar Co. Ltd.
Standard Analytical Procedures

LAB. AFFINATION

Principle. — To evaluate the affinability of various raw sugars, that is, the efficiency of non-sugar removal by affination, raw sugar and a saturated pure sugar solution are blended in given proportions, and the excess syrup separated by centrifugation under standardized conditions.

The resulting sugar is the equivalent of ideal washed raw sugar.

Equipment. — (1) Philips mixer, Model KB100, manufactured by Philips Appliances Ltd., Leaside, Ontario; (2) International Chemical Centrifuge with 5 inch diameter basket lined with a perforated screen .007 inch circular opening, .007 inch thickness and 29 percent open area; (3) Sprayer 125 ml capacity. Fisher Scientific Catalogue No. 5-719-5; (4) Rubber spatula.

Reagents. — (1) Pure sucrose solution, 67.6 Brix (obtained from liquid sugar station).

Procedure. — (1) Weigh 400 g. raw sugar and put in bowl of mixer; (2) Add 200 g. 67.6 Brix sugar solution at room temperature; (3) Stir for 5 minutes at speed "5"; (4) Transfer complete contents into the centrifuge basket using a rubber spatula for cleaning the bowl; (5) Turn centrifuge to full speed, and start timer; (6) After 2.5 min., spray 5.6 cc of water into the spinning sugar (1.4 percent water on crystal); (7) Stop centrifuge after 5 minutes of total spinning time; (8) Remove sugar and mix thoroughly.

APPENDIX B

Laboratory Affination of Raw Sugars

1966 — 1967

Cargo Number	Pol	Chlorides, Percent on solids			Ash, Percent			Invert, Percent			Colour Units			$CaCO_3$, Pct. on solids			K, p.p.m.			Na, p.p.m.		
		Raw	WSL	Pct. Rem	Raw	WSL	Pct. Rem	Raw	WSL	Pct. Rem	Raw	WSL	Pct. Rem	Raw	WSL	Pct. Rem	Raw	WSL	Pct. Rem	Raw	WSL	Pct. Rem
1.	97.83	.0924	.0050	92.2	.61	.10	83.6	.38	.05	86.9	5060	852	83.2	.2050	.0396	80.7	1600	186	88.4	34.5	5.0	85.5
2.	98.50	.0466	.0046	90.1	.31	.07	77.4	.52	.16	69.2	1780	448	74.8	.1300	.0366	71.8	800	148	81.5	14.5	3.8	73.8
3.	98.62	.0434	.0044	89.9	.34	.08	76.5	.40	.13	67.5	2640	672	74.5	.1640	.0438	73.3	920	164	82.2	19.5	4.6	75.4
4.	97.94	.0682	.0059	91.3	.48	.09	81.3	.71	.15	78.9	2620	564	78.5	.1700	.0414	75.6	1140	160	86.0	20.5	3.9	81.0
5.	97.72	.0422	.0038	91.0	.43	.10	76.7	.73	.16	78.1	3000	648	78.4	.2075	.0626	69.8	700	92	86.9	21.5	4.4	79.5
6.	96.82	.0648	.0054	91.7	.50	.07	86.0	1.16	.20	82.8	3300	694	81.4	.2030	.0490	75.9	1100	116	89.5	41.5	9.6	76.9
7.	96.67	.0593	.0038	93.6	.50	.09	82.0	1.37	.15	89.1	4300	712	83.4	.1735	.0340	80.4	1200	136	88.7	35.0	3.8	89.1
8.	96.89	.0591	.0034	94.2	.52	.05	90.4	1.31	.12	90.8	4500	832	81.5	.1770	.0364	79.4	1240	138	88.9	24.5	3.6	85.3
9.	97.45	.0603	.0043	92.9	.49	.09	81.6	1.06	.10	90.6	3120	764	75.5	.1970	.0532	73.0	880	90	89.8	31.5	5.0	84.1
10.	97.01	.0262	.0022	90.9	.41	.08	80.5	1.06	.44	58.5	3020	676	77.6	.1540	.0410	73.4	780	102	86.9	11.5	2.8	75.7
11.	98.80	.0402	.0043	86.5	.34	.10	70.6	.18	.08	55.6	2260	524	76.8	.1475	.0522	64.6	620	94	84.8	18.0	4.6	74.4
12.	97.10	.0902	.0082	90.9	.60	.14	76.7	.89	.15	83.1	3100	632	79.9	.1825	.0526	71.2	1380	238	82.8	53.0	8.8	83.4
13.	97.54	.0565	.0060	89.4	.50	.13	75.0	.71	.16	77.5	3780	996	73.7	.1750	.0600	65.7	1120	222	80.2	24.5	6.4	73.9
14.	97.40	.0415	.0048	88.5	.41	.10	75.6	.82	.16	80.5	3560	956	73.1	.2000	.0592	70.4	860	84	90.2	20.5	4.2	79.5
15.	96.51	.1028	.0099	93.7	.62	.12	80.6	1.38	.20	85.5	3180	726	77.2	.2175	.0530	75.6	860	166	80.7	103.0	12.8	87.6
16.	97.70	.0333	.0047	85.9	.41	.13	68.3	.87	.17	80.5	3400	916	73.1	.1785	.0335	81.3	1380	84	93.9	23.5	5.0	78.7

Cargo Number	Pol	Chlorides, Percent on solids			Ash, Percent			Invert, Percent			Colour Units			$CaCO_3$, Pct. on solids			K, p.p.m.			Na, p.p.m.		
		Raw	WSL	Pct. Rem	Raw	WSL	Pct. Rem	Raw	WSL	Pct. Rem	Raw	WSL	Pct. Rem	Raw	WSL	Pct. Rem	Raw	WSL	Pct. Rem	Raw	WSL	Pct. Rem
17.	96.68	.0941	.0072	92.3	.59	.10	83.1	1.21	.18	85.1	3700	688	81.4	.2050	.0610	70.2	620	178	71.3	69.0	8.2	88.1
18.	98.77	.0512	.0038	92.6	.36	.07	80.6	.31	.09	71.0	2200	556	74.7	.1120	.0715	36.2	1340	132	90.1	18.5	3.0	83.8
19.	98.79	.0575	.0032	94.4	.33	.05	84.8	.34	.08	76.5	2800	300	89.3	.1150	.0238	79.4	980	94	90.4	24.0	3.0	78.5
20.	97.87	.0384	.0035	90.9	.45	.13	71.1	.73	.13	82.2	3260	616	81.1	.1790	.0640	64.3	920	104	88.7	20.5	3.8	81.5
21.	98.07	.0520	.0062	88.1	.49	.14	71.4	.74	.18	75.7	3580	836	76.6	.1575	.0533	66.2	760	248	67.4	25.0	5.6	77.6
22.	98.93	.0411	.0069	83.2	.31	.14	54.8	.29	.09	69.0	1640	732	55.4	.1175	.0505	68.0	1120	196	82.5	9.5	3.4	67.4
23.	96.52	.0592	.0058	90.2	.47	.12	74.5	1.23	.21	74.5	3860	720	82.2	.1687	.0408	76.9	700	142	79.7	30.5	4.4	85.6
24.	99.03	.0454	.0061	86.6	.30	.07	76.7	.21	.09	52.4	2000	620	69.0	.1095	.0301	72.5	1020	126	87.6	22.5	3.6	84.0
25.	96.84	.1020	.0085	90.0	.64	.12	81.3	.67	.17	74.6	5600	608	89.1	.2225	.0505	78.0	760	172	77.4	66.0	7.8	88.2
26.	99.18	.0120	.0031	74.2	.20	.08	60.0	.18	.10	44.4	1260	480	61.9	.0665	.0209	68.5	1440	138	90.4	9.5	2.6	72.6
27.	98.75	.0408	.0042	89.7	.32	.10	68.8	.34	.11	67.6	1840	503	72.7	.1225	.0403	67.1	529	138	73.5	18.5	3.0	83.8
28.	98.34	.0477	.0051	89.3	.35	.09	74.3	.31	.09	71.0	2240	700	68.8	.1400	.0401	71.4	700	116	83.4	18.5	3.2	82.7
29.	98.79	.0460	.0063	86.3	.35	.07	80.0	.25	.09	64.0	2220	680	69.4	.1110	.0302	72.8	740	124	83.2	19.0	3.8	80.0
30.	98.71	.0520	.0058	88.8	.46	.07	59.1	.22	.09	59.1	1520	607	60.1	.1108	.0320	71.1	740	114	84.6	18.0	3.2	82.2
31.	98.69	.0489	.0050	87.9	.36	.08	78.0	.29	.10	65.5	1840	480	73.9	.1305	.0307	76.5	760	114	85.0	16.5	4.2	72.7
32.	98.70	.0433	.0048	88.9	.44	.11	75.0	.31	.08	74.2	2200	520	76.4	.162	.054	66.7	960	82	91.4	29	7.8	73.1
33.	97.40	.0403	.0042	89.6	.38	.08	78.9	.86	.09	89.5	2840	640	77.5	.170	.048	71.8	640	72	87.2	28	6.2	77.8
34.	97.35	.0772	.0072	90.7	.56	.12	78.6	.91	.09	90.1	2540	608	76.1	.197	.055	72.1	1260	190	84.9	73	9.8	86.5
35.	97.45	.0784	.0076	90.3	.59	.11	81.4	.78	.08	89.7	3500	780	77.7	.212	.056	73.6	1460	184	87.5	41	7.6	81.4

Cargo Number	Pol	Chlorides, Percent on solids			Ash, Percent			Invert, Percent			Colour Units			$CaCO_3$, Pct. on solids			K, p.p.m.			Na, p.p.m.		
		Raw	WSL	Pct. Rem	Raw	WSL	Pct. Rem	Raw	WSL	Pct. Rem	Raw	WSL	Pct. Rem	Raw	WSL	Pct. Rem	Raw	WSL	Pct. Rem	Raw	WSL	Pct. Rem
36.	98.85	.0490	.0069	85.9	.34	.08	76.5	.24	.03	87.5	2640	520	80.3	.140	.044	68.6	780	188	76.0	25	7.2	71.3
37.	97.20	.0339	.0027	92.0	.37	.08	78.4	.95	.12	87.4	3600	688	80.9	.182	.049	73.1	600	74	87.8	29	6.6	77.3
38.	97.35	.0721	.0047	93.5	.54	.09	83.4	.78	.31	60.3	4140	620	85.0	.195	.050	74.4	1420	168	88.1	34	6.2	81.8
39.	96.70	.0954	.0079	91.7	.64	.13	79.8	1.08	.14	87.0	3300	680	79.4	.250	.062	75.2	1520	196	78.2	89	11.2	87.4
40.	97.30	.0560	.0034	93.9	.36	.13	64.0	.86	.13	84.9	3260	620	81.0	.180	.059	67.2	860	138	84.0	39	7.8	80.0
41.	96.05	.0701	.0050	92.9	.68	.08	88.2	1.43	.48	66.5	11200	500	95.5	.230	.041	82.2	1700	194	88.5	46.5	7.2	84.5
42.	96.62	.0827	.0077	90.7	.56	.12	78.7	1.12	.58	48.2	6200	288	95.4	.210	.057	72.8	1440	200	86.1	75	12.4	83.5
43.	98.70	.0423	.0041	90.3	.30	.10	66.7	.34	.02	94.2	2000	280	86.0	.130	.044	66.2	820	122	85.1	28.5	9.8	65.6
44.	96.37	.0632	.0040	93.7	.55	.11	80.0	1.15	.08	93.2	5000	168	96.6	.250	.061	75.6	1000	100	90.0	35	8.8	74.9
45.	97.20	.0325	.0033	89.8	.32	.09	72.0	.47	.06	87.2	2400	180	92.5	.110	.036	67.3	920	166	81.9	21	5.6	73.3
46.	98.65	.0290	.0036	87.6	.37	.11	70.3	.36	.05	86.2	2200	172	92.2	.105	.038	63.8	340	188	80.0	23	6.6	71.4
47.	96.90	.0690	.0044	93.6	.42	.11	73.8	.90	.08	91.1	4500	160	96.4	.167	.051	69.5	1000	128	78.2	85	15.0	82.3
48.	98.35	.0305	.0042	86.2	.25	.10	60.0	.42	.03	92.9	2700	224	91.7	.105	.039	62.8	940	166	82.1	23.5	7.2	69.4
49.	98.77	.0400	.0028	93.0	.37	.09	75.7	.21	.04	81.0	1860	196	89.5	.112	.031	72.4	800	86	84.2	24.5	2.9	90.7
50.	98.32	.0292	.0033	88.7	.30	.09	70.0	.32	.05	84.5	2600	100	96.2	.112	.038	66.1	740	166	77.5	22.5	6.2	72.5

APPENDIX C

Reliability of Analytical Methods
Raw Sugar

	Mean Value	Standard Error	95 percent confidence limits
Cl percent	.0516	.0005	± .0001
$CaCO_3$ percent	.1079	.0009	± .0002
Na percent	.0035	.0004	± .0005
K percent	.1520	.0024	± .0018

APPENDIX D

Canada & Dominion Sugar Co., Ltd.
Standard Analytical Procedures

CHLORIDE DETERMINATION

Principle

Cl^- in solution is potentiometrically titrated with $AgNO_3$, using a silver electrode as an indicator. The titration is automatically stopped at the end point by means of a magnetic valve, operated by a titrator.

The theory of this method is as follows. When a silver electrode is emerged in a solution containing Ag^+ ions, an equilibrium involving the transfer of electrons is established:

$$Ag \rightleftharpoons Ag^+ + 1\,e^-$$

This equilibrium is reached either by dissolution of a minute amount of metal, or by the deposition of the ion on the electrode. In the first case, a negative charge builds up on the electrode as positive Ag^+ ions leave it to dissolve; in the second case, if the ions deposit on the electrode, a positive charge appears.

In either event, the reaction is limited by the charge that accumulates at the electrode. This charge depends on the concentration of ions in solution and the electric potential it creates varies according to:—

$$E = E_0 + 0.06 \log [A^+]$$

$$= 0.80 + 0.06 \log [A^+]$$

Where: E = potential in volts assumed by the electrode

E_0 = potential when the concentration of ions is made unity (one molar)

In a solution containing Cl^- ions, the addition of Ag^+ ions will give a silver chloride precipitate as follows:

$$Cl^- + Ag^+ \rightleftharpoons AgCl.$$

As long as there is an excess of chloride present, the measured potential will be small and fairly steady.

However, near the equivalence point, a small addition of silver nitrate will cause a sudden change in the Ag^+ ion concentration, and the potential will raise. With appropriate setting of the automatic titrator, the magnetic valve will stop the flow of silver nitrate at the end point.

Equipment

(a) Automatic Titrator Assembly TTT1, Radiometer

(b) Magnetic valve MNVIC, Radiometer

(c) Electrode K601 and P501, Radiometer

(d) Balance, Sartorius 2205, or Mettler P120 Capacity 160 g. Sensitivity 2 mg.

(e) Burette Automatic Machlett 10 ml.

(f) Magnetic stirrer with stirrer bar

(g) Beakers 250 ml.

(h) Volumetric flask 1000 ml.

(i) Volumetric flask 100 ml.

Reagents

(a) Silver nitrate
4.7860 g. of $AgNO_3$ are dissolved in deionized water in a 1000 ml. volumetric flask and made up to mark. This solution is stable for some months when stored in a dark bottle. 1 ml. of this solution is equivalent to 1 mg. of Cl^-.

(b) Standard Cl^- solution
0.5846 g. of dried NaCl is dissolved in deionized water in a 100 ml. volumetric flask and made up to mark. 10 ml. of this solution is equivalent to 3.545 mg. of Cl^- (Must be done on an analytical balance of 1/10 mg. sensitivity).

Procedure

Titrator settings:	End point	+ 100 mV
	Range	0
	Delay of shut-off	15”
	Proportional band	2

(a) Weigh out adequate quantity of sample (See table 1) directly in tared 250 ml. beaker.

(b) Add about 50 ml. of deionized water, directly in beaker and drop magnetic stirrer bar in solution.

(c) Put beaker on magnetic stirrer and stir until an homogeneous solution is obtained.

(d) Run titrator with automatic titrator and repeat the entire procedure three times. Take average titration value for final calculation.

Calculation

Assume sample weight was	: 10 g.
Assume sample Brix was	: 73.5
Assume end point was	: 4.25 ml. $AgNO_3$
Assume $AgNO_3$ standardized exactly as 1 ml.	: 1 mg. Cl^-

Cl^- content percent solids =

$$\frac{.00425 \times 100 \times 100}{10 \times 73.5}$$

= .058 percent

Standardization

(a) Pipette 20 ml. of standard Cl^- solution into beaker.

(b) Add deionized water to cover electrodes.

(c) Stir with magnetic stirrer assembly and titrate with titrator. Repeat procedure three (3) times, and record average titration result.

Calculation

Assume end point was : 7.09 ml.

Equivalency of 1 ml. of $AgNO_3$ will be : $\frac{20 \times .3545}{7.09}$

: 1 ml. Cl^-

Table 1

Sample	Recommended weight
Raw sugar	10 g.
Washed raw sugar	30 g.
Raw syrup	0.5 — 1 g.
Mingling syrup	1 g.
Magma	2 g.
Wash water	5 g.

DISCUSSION

A. VanHOOK: When you calculate the ionic strength of the ions in the sugar solution, do you use the total volume of the solution, or just the apparent volume of the water in that solution?

P. POMMEZ: I use the apparent volume of the water in the solution.

A. VanHOOK: Do these electrodes have much of an asymmetry potential; that is the intercept on your potential vs. chloride concentration curve? You've got a very nice slope, 59 — just about on the nose. What about the intercept which is referred to as the asymmetry potential. If you make silver — silver chloride electrodes, for instance, yourself, I believe that every other one has a slightly different potential, by a few millivolts, and this difference is referred to as the asymmetry potential.

J. TAYLOR: There is really no such thing as a correct intercept for this electrode. This is a silver chloride-mixed sulfide membrane, which is now made in a solid state configuration. There are no internal filling solutions at all. The electrode has been revised since the diagrams which are shown in Figure 2. So the intercept of the line — in terms of asymmetry potentials for pH electrodes — is not really valid for ion-selective electrodes of this designation. The absolute potential doesn't really matter, and will vary from day to day. The only thing that really matters in terms of the validity of the measurements is the slope of the line. The intercept depends on the total capacity of the electrode system, and the resistance of the particular material used in the membrane.

A. VanHOOK: Then each electrode must be individually calibrated?

P. POMMEZ: That's right. Thank you, Mrs. Taylor.

E.C. MULLER: You said that in examining about a hundred raw sugars, you found recovery of almost 90 percent, using the chloride test. How does that percentage recovery vary with raw sugars of different purity? If you have one raw sugar which is very much less pure than another, do you get a different recovery percentage?

S. STACHENKO: We have found that chloride removal from raw sugar by the standard affination procedure is reasonably constant regardless of the quality of the raw sugar. As an example, the standard deviation for chloride removal is 3 percent, even though raw sugars which were used to establish the standard deviation were varying in polarization from 96 to 99 plus. In Appendix B you will find, documented in detail, the comparative analysis of all raw sugars before and after affination, and thus you may verify directly the chloride removal efficiency as a function of raw sugar. I should also mention that the 3 percent standard deviation represents the lowest standard deviation of any impurity removal by the standard affination process, thus indicating its particular value.

J.A. METZLER: Is there any reason why you couldn't use potassium or sodium instead of chloride for affination control?

P. POMMEZ: I think you could use potassium or sodium. We have followed closely the removal of potassium and sodium in the affination process, and we have found that the potassium or sodium removal was very close to the chloride values. Even for the standard deviation, we got very good values for the percent removal of potassium and sodium. The problem is that, to detect potassium or sodium we have to use flame photometry, and we could have some interference. As you know, sodium interferes with potassium in the determination of potassium by flame photometry. It may be possible to use some ion-selective electrodes for potassium or sodium — I believe there are some which came on the market last year.

J.L. De CHAZAL: You mention the 90 percent chloride ion removal as the measure of your affination station efficiency. You measured between the magma and the washed sugar liquor. In the case of the magma, do you have to dissolve the crystals, in other words bring them down to 60 Brix or so, or can you use the electrode right in the magma as is?

P. POMMEZ: If you want to have a differential measurement, the best way to obtain that would be to put another chloride ion electrode in the melting water and measure the differences in millivolt reading between that electrode and the electrode after the affination station.

S. STACHENKO: First of all, I would like to make it quite clear that when we talk of 90 percent removal of chloride we are talking of the elimination of chloride from raw sugar and not from the raw magma. Of course, one of the problems which might occur in trying to control directly the wash setting as a function of chloride content in the washed raw sugar, is the fact that in practice it is rather difficult to have a representative sample of the washed raw sugar in solid form and one would prefer to use the melter liquor as the average sample relating to the quality of the washed raw sugar. This is fine as long as one is using pure water for melting, but if the composition of the melting water varies fairly drastically because of the use of various sweet waters, the chloride content of the melting water itself could influence the chloride content of the washed sugar liquor, independently of the quality of the washed raw sugar. One relatively easy way to solve this problem is to take a differential measure between the melting water supply and the melter liquor, thus obtaining continuously a net chloride reading for the washed raw sugar only.

C.C. CHOU: Would you care to comment on the manner in which the sucrose molecules affect the electrode potential? Is the effect due to the change in dielectric constant, or due to the specific adsorption on the electrode surface, or due to solvation of the chloride ion by the sugar molecule?

P. POMMEZ: We don't know exactly what happens. I think the effect could be due, as a first approximation, to some attraction of the sucrose, at a certain Brix, for the water molecule, which would change the amount of water at the disposal of the chloride ion, and thus change the concentration of the ion. At this point, I don't think there is any inclusion of sodium chloride or any reaction with sucrose in solution. However, in the low (10 to 20) Brix region, we repeatedly observed a lower millivolt reading (i.e. higher chloride concentration) than was expected from the calculated value (calculated on the apparent volume of water). It is suggested that in this particular range of sucrose concentration, the sucrose-water ratio could be favorable to the formation of sucrose hydrate complexes.

C.C. CHOU: In equation 5 you showed the activity of chloride ions depending on the concentration only. This is generally true in diluted aqueous solution, but I think in sucrose solutions you would have to modify the equation to take into account the change of dielectric constant, etc.

P. POMMEZ: Yes, in the Debye-Huckel equation, we should change the factor which is generally used for water to the factor for the particular sucrose solution.

A. VanHOOK: I think the dielectric constant of sugar solutions does not change much upon the addition of electrolyte. I don't have the exact figures, but I know I looked at that one time, and there was no specific influence. I think in the theory, when you get into the extended Debye-Huckel calculation, you go right along using the dielectric properties of the solvent — water in this case — regardless of the addition of electrolytes.

C.C. CHOU: I am not too concerned about the dielectric constant in the bulk solution. As you probably know, the dielectric constant in the vicinity of the electrode, in the case of an aqueous solution, may range from 6 to 15, while it is about 80 in the bulk solution. I am wondering about the possible effect of sucrose adsorption on the dielectric constant of sucrose solution in the vicinity of the electrode.

P. POMMEZ: I have no answer at this time.

THIRD SESSION: Charles T. Dickert, Rohm and Haas Co., Chairman

PROPERTIES OF SUGAR COLORANTS REMOVABLE BY ION-EXCHANGE RESINS

by

D. Cookson, K. J. Parker, and J. C. Williams
Tate and Lyle Research Centre
Keston, Kent, England

(Presented by E. C. Muller
Tate and Lyle Refineries Ltd.
London, England)

ABSTRACT

Up to 95 percent of the coloring matter of washed raw sugar is removable by ion-exchange resins. Part of this is anionic, the colorant being a polybasic carboxylic acid. It may be fractionated on ion-exchange cellulose according to the net anionic charge. The molecular size distribution of the colour is determined by gel filtrations. These properties give an indication of the decolorisation by, and ease of regeneration of, anion-exchange resins.

Decolorisation is also effected by matrix adsorption on polystyrene resins. Colorant, including amphiprotic colour, having no net anionic charge, is retained by this mechanism. Zwitterionic colour is highly polar, and having no net charge, is not retained by any resin now commercially available.

INTRODUCTION

Although the coloured impurities of raw sugar represent only a small proportion of the total non-sugars, their removal is one of the most important functions of sugar refining. In order to obtain optimum efficiency from any decolorising process, be it by flocculation, decolorising carbon, bone char or ion-exchange resins, a knowledge of the nature and behaviour of the colorants is essential.

Part of the colour of refinery liquors is due to the presence in raw sugar of naturally occurring coloured impurities extracted from the beet or cane. The remainder comprises the mixture of colorants produced in the degradation of sugars during successive extraction and refining processes. It is this wide range of coloured decomposition products of reducing sugars, readily formed at high temperatures and pH and especially in the presence of amino acids, which are most amenable to removal by ion-exchange resins.

The development of methods for isolation and examination of these sugar colorants has been guided by results obtained from a study of synthetic colorants produced under conditions similar to those in the factory. These were originally developed as reproducible standard colorant solutions for use in the routine assessment of ion-exchange resin decolorisation performance. Subsequent work has shown that these colorants do correspond in all the properties so far examined with fractions isolated from sugar liquors.

Three standard colorant preparations have been used:

(1) Anionic colorant (glucose colour); prepared by boiling a 2 percent glucose solution at pH 9.5 (controlled by a pH stat) for 5 hr. After cooling, the pH is adjusted to 7.5.

(2) Weakly basic amphoteric colorant (glycine colour); similarly prepared but with the addition of glycine (0.1 M).

(3) Strongly basic amphoteric colorant (lysine colour); similarly prepared but with the addition of lysine (0.1 M).

ISOLATION OF COLORANTS

Any method used to isolate colorants needs to be mild to avoid chemical modification. Initially, complete nonselective isolation is also desirable. Two methods have been developed which are generally applicable, giving up to 95 percent recovery of colour from raw sugar.

(1) A column of Amberlite resin XAD-2 (a hydrated polystyrene) readily retains colorants at pH 2 - 3 but rejects sugars and inorganic salts. Partial desorption is accomplished by washing with methanol, and the colorant (referred to as the Y fraction) is obtained in solid form by evaporation of the solvent. Colorant remaining on the resin (Z fraction) is removed by washing with N/100 hydrogen chloride in methanol, and recovered as a solid by precipitation with benzene. This method is ideally suited to the recovery of colorants from very dilute solutions in sugar liquors, as concentration is effected during the passage of large volumes of liquor.

(2) An alternative method, which is more selective, involves the precipitation of the colorant at pH 7 with an aqueous solution of cetyltrimethyl ammonium bromide (CTAB) or dioctadecyl dimethyl ammonium chloride. The precipitated colorant surfactant coacervate may be water washed and dried. The potassium salt of the colorant is precipitated from an ethanolic solution of the coacervate with potassium bromide.

PROPERTIES OF COLORANTS

Generally, the colorant does not have a definite or constant molecular composition or exactly reproducible properties. Consequently, the usual criteria of purity cannot be applied and no attempt has been made to obtain a pure fraction.

The various properties have been examined with the object of relating them to the molecular structure of the colorant and to the behaviour of the colorant towards adsorbents. The properties examined were the spectra, the distribution of ionisable groups, molecular size and net anionic charge.

Absorption spectra. — The most readily studied property of colour is, of course, the visible adsorption spectrum. A singular feature is the consistency of the relationship between absorbance (A_λ) and the wavelength (λ) at which it is measured. This is given by the equation:

$$A_\lambda \cdot \lambda^n = K$$

This is independent of the concentration of the colorant, the wavelength index being a characteristic property.

A related parameter, the N-value, more convenient to use in practice, is $N = 100 \left(\frac{A_{520}}{A_{455}} \right)^2$.

It is related to the wavelength index (n) by[1]: $n = 8.58\ (2 - \log_{10} N)$. Its value normally lies between 5 and 50 and thus constitutes a convenient scale by which to characterise the colorant.

The N-value is related to the proportion and extent of conjugation of unsaturated centres in the colorant polymer. The probability of extended conjugation increases with increase in polymer length. Consequently, N-value is an indication of colorant molecular weight, low N-value being associated with low molecular weight.

The specific absorbances (at 455 nm.) and N-values of colorants isolated from different sources are given in table 1.

It is notable that the specific absorbance of the various types of colour shows surprisingly little difference. It shows that the much greater colour development in the presence of amino-acids is due, not so much to colour of high intensity, but to a larger quantity of coloured compounds being formed.

The ultraviolet spectrum of the colorant tends to be uninformative, owing to the intense absorption at shorter wavelengths due to ethylenic and carbonyl unsaturation. The frequently observed maximum at around 265 nm. is due to the superimposition of the spectrum of monomeric colour precursors.[2]

The infrared spectra of colorants isolated from diverse sources and having dissimilar properties are at first sight remarkably similar. The spectra are poorly resolved and further fractionation of the colorant has not improved this.

The isolated colorants themselves, being insoluble in the commonly used infra-red solvents, have to be examined as potassium bromide discs. Some derivatives however (acetates, esters) are soluble in chloroform and may be examined in solution. Close examination of the spectra of the colorants and their derivatives reveals small differences which throw light upon their general chemical structures.

Table 1. — Specific absorbance and N-value of isolated fractions of colour from different sources

	Glucose	Glycine	Lysine	Lysine	Raw cane
Colorant	Y	Y	Y	Z	Y
Specific absorbance	2100	2430	1110	3310	2420
N-value	24	37	22	44	28

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[1] Parker, K. J. 1967. The measurement of the colour of sugar solutions. Proc. 1966 Tech. Sess. Cane Sugar Refin. Res. 72-84.

[2] Parker, K. J. 1970. Chemical problems in the sucrose industry. La Sucrerie Belge 89: 119-126.

The broad absorption band centered around 3400 cm.$^{-1}$ is characteristic of all colorants and is attributed to hydroxyl groups (and also to amino groups in some Maillard colorants). This disappears or is reduced upon acetylation when new bands appear in the C = O stretching region around 1740 cm.$^{-1}$ due to acetate, and also in Maillard colorants around 1670 cm.$^{-1}$ due to amides. Acetylation of glucose colorant also gives an absorption attributed to the enol acetate group at 1771 cm.$^{-1}$.

Small C - H stretching absorptions occur around 2930 cm.$^{-1}$ which are enhanced in the derivatives. They have a long "tail" to about 2200 cm.$^{-1}$ due to hydrogen bonded carboxyl groups. This tail disappears on esterification.

In the 1600 to 1800 cm.$^{-1}$ region, bands occur which are attributed to α,β-unsaturated carboxyl (1709 cm.$^{-1}$) and conjugated carbon-carbon double bonds (1625 cm.$^{-1}$), the former shifting on esterification to 1730 cm.$^{-1}$.

Maillard type colorants show a characteristic absorption (often a definite peak) in the 1510 to 1520 cm.$^{-1}$ region which disappears on acetylation and also, in the case of lysine colorant, upon deamination with nitrous acid. This is obviously associated with a nitrogenous function but has not yet been definitely assigned.

A detailed comparison of spectra of lysine Y and Z fractions confirms their suspected Zwitterionic nature, lower in the Z fraction, the broad absorption at 1628 cm.$^{-1}$ being attributed to $-NH_3{}^+$ deformation. This confirms the suspected participation of the lysine (with its two amino functions) in a cross-linking reaction to form the higher molecular weight Z material. The methyl esters of lysine Y and Z colorants have identical spectra, having a single ester function and un-ionised NH_2 group (1642 cm.$^{-1}$). After bromination, colorant shows evidence of addition to the double-bond (reduction in 1625 cm.$^{-1}$ intensity) and substitution of bromine α- to a carboxyl (shift from 1709 to 1728 cm.$^{-1}$).

Distribution of basic groups. — Even 100 percent anionic colorant is adsorbed by strong cation exchange resins from aqueous solutions at low pH. This is attributed to adsorption on the resin matrix, and is wholly suppressed in methanolic solution. Colorant to be examined for its content of basic groups (in its acid form) is dissolved in methanol at pH 2 and passed through a column of Amberlite 200 (a macroreticular cation exchanger, in the H^+ form). Purely anionic material is not adsorbed. Colorants with basic functions are adsorbed and may then be desorbed in ascending order of their base strength by elution with aqueous alkali. Some of the distributions obtained are shown in figure 1.

The increasing contents of more basic material in the series: glucose, glycine, lysine colorants is expected. The liquor shown is unusual in having no weakly basic colorant. Other liquors give a pattern more like that of molasses. Purely anionic colour is not adsorbed by the resin and passes straight through the column. Elution with aqueous alkali of increasing pH displaces adsorbed colorant in order of basic strength.

Anionic charge density. — Polyanions are precipitated from solution by long-chain alkyl quaternary ammonium ions. Similarly, polymeric cations are precipitated by anionic surfactants. Amphoteric colorant is found to be precipitated from aqueous solution at the appropriate pH by either hexadecyl ammonium bromide (CTAB) or sodium dodecyl sulphate.

When the anionic charge of a colorant arises from the ionisation of acids of different basicity, charge density will be a function of pH. Colorant derived from the alkaline degradation of reducing sugars displays a progressive increase in charge density with increase in pH up to 10. This is very much less pronounced in the amphoteric Maillard colorants. This is interpreted as indicating the participation of enolic ionisation in the former case, while in the latter, potential enolic groups have reacted with amines and are no longer ionisable. This would account for the indicator effect observed with anionic colorant but not with Maillard colorant.

The result of titrating solutions of colorants with aqueous CTAB, measuring the turbidity at the red end of the spectrum, is shown in figure 2. The dependence of anionic charge density on pH is greater for glucose colour than for Maillard colour.

Molecular size and molecular weight. — Homogeneous fractions of colorant have not yet been separated, so the usual methods of molecular weight determination are not applicable. Gel permeation is a technique which has previously been applied to the fractionation of sugar colorants according to molecular weight[3]. However, adsorptive retention (attributed to hydrogen bonding) of the colorant by the gel matrix has led to doubt concerning the interpretation of the results.

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[3] Smith, N. H. 1967. Fractionation of sugar colorants with molecular sieves. Proc. 1966 Tech. Sess. Cane Sugar Refin. Res. 84-102.

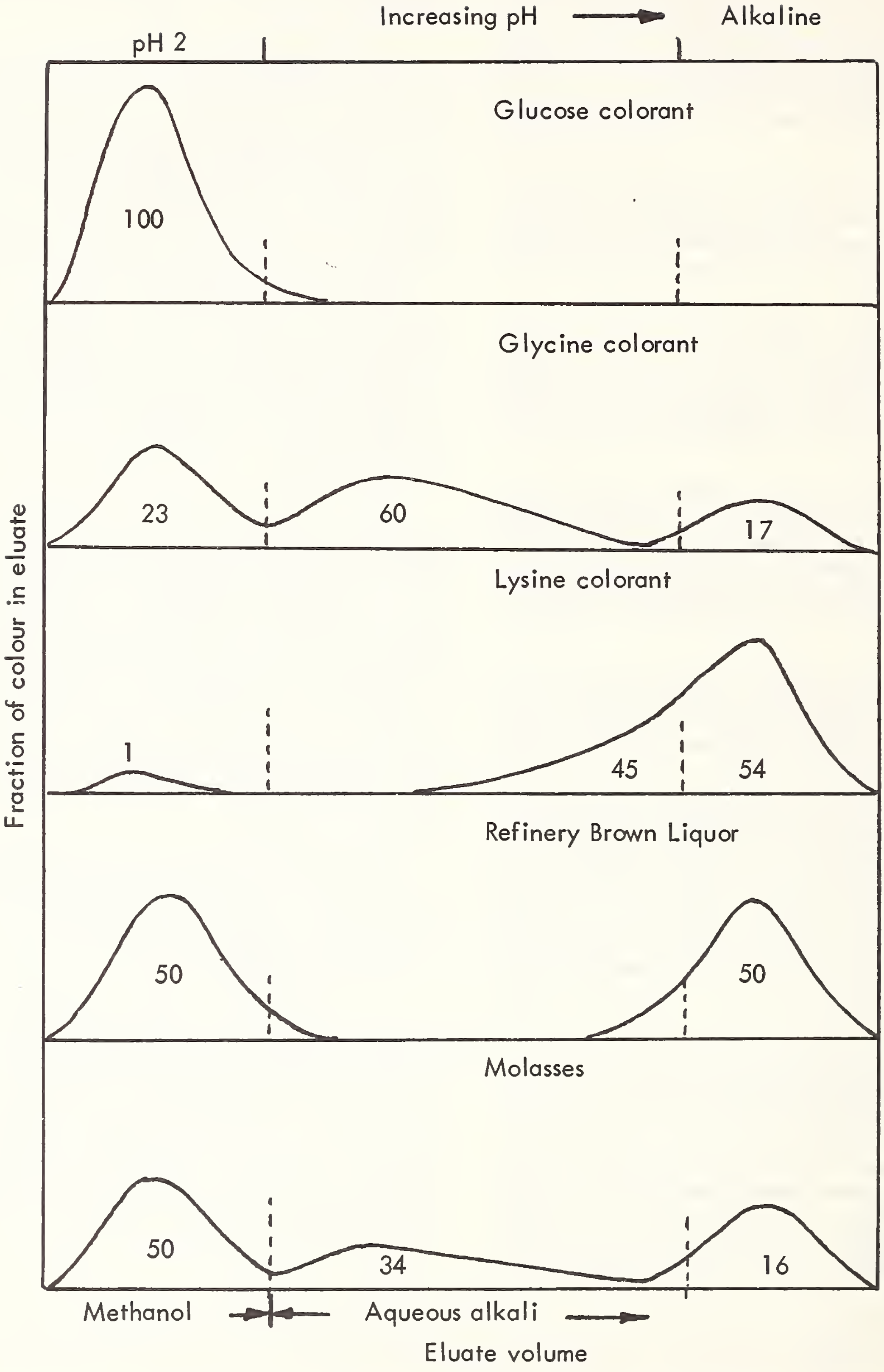

Figure 1. — Colorant composition as a function of base strength.

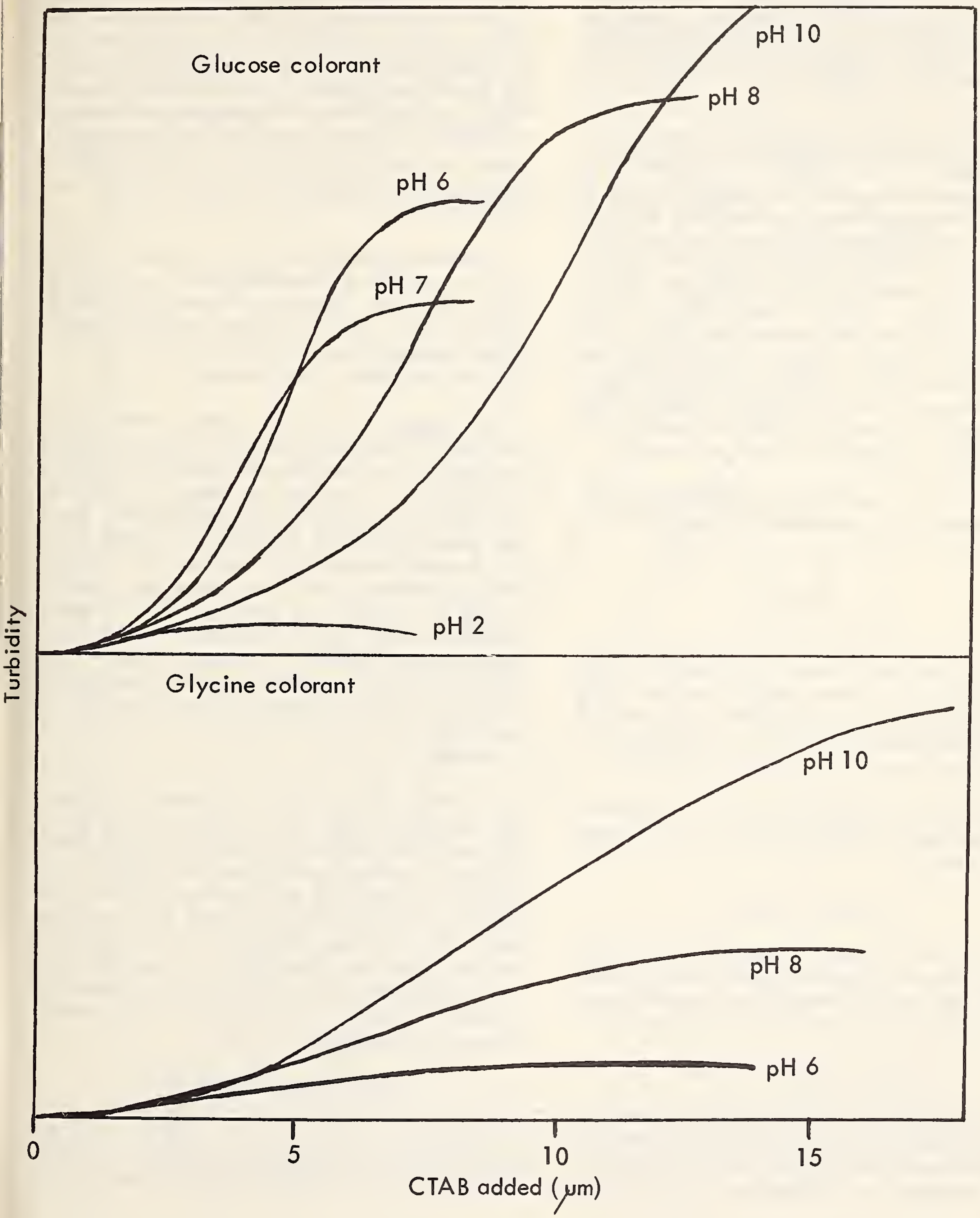

Figure 2. — Precipitation of colorant with CTAB as a function of pH (indicated).

We have found that adsorption is almost completely prevented if gel permeation is carried out on Sephadex (G 25 or G 50) in 8M urea solution, buffered at pH 7.5 with 0.01 M triethanolamine hydrochloride. This has led to the development of a routine automated method for determining the molecular size distribution of colorants in solution, applicable even to refinery fine liquors.

The effluent from a Sephadex column (35 cm. x 2.5 cm. diam.) is led through a flow-cell in a spectrophotometer, the electrical output of which is amplified and integrated using a Honeywell precision integrator to give a digital printout of the cumulative colour over 5 minute intervals. Sensitivity is 500 counts for 0.01 absorbance units. Base line stability can be ±5 counts. Although density changes in the flow cell can interfere with measurements, colorants in liquors may be examined because the relatively large amount of sucrose present does not emerge until well after the maximum in molecular size distribution has been reached. To date, the least coloured liquor examined had an absorbance of 0.1 in a 1 cm. cell.

The separation of molecules by gel permeation may be characterised by the parameter K_{av}, defined by:

$$K_{av} = \frac{V_e - V_o}{V_t - V_o}$$

where Vo is the void volume of the column, i.e. the elution volume of a totally excluded substance (e.g. blue dextran, mol. wt. ~ 2,000,000). V_t is the total volume of the gel bed, i.e. the column dimensions. V_e is the elution volume of the solution as measured.

Laurent and Killander[4] derive a relationship between K_{av} and the effective radius (r) of a solute molecule given by:

$$K_{av} = \exp(-\pi L(r+a)^2).$$

L and a are constants characteristic of the gel network obtained by calibration with solutes of known molecular size. In the present study, using Sephadex G25, the effective molecular radius (Å) is given by:

$$r = 12.83\,(-\ln K_{av})^{1/2} - 4.13.$$

The molecular size distribution of synthetic and liquor colorants is shown in figure 3 as a cumulative size distribution. Glucose colour is found to have the lowest molecular size distribution. The enhanced efficiency of glucose degradation in the presence of glycine results in molecular sizes greater than those of glucose colorant, while the cross-linking which can occur in the presence of lysine gives colorants of still higher molecular weight. The sample of liquor colorant is seen to fall well within the range of sizes found in the synthetic colorants. In these figures, K_{av} values <0 are due to axial diffusion in the Sephadex columns. Values near 0.7 (the value for glucose) must be treated with caution as some adsorption is occurring. The N-values of colorants eluted from Sephadex columns confirm the relationship between N-value and molecular weight.

Molecular size distributions are obviously of direct value in considering decolorisation by ion exchange resins when the controlling factor is access to adsorption sites. Should molecular weights be needed, further calculations are necessary, taking into account the molecular shapes of the colorants.

Net charge. Ion-exchange resins, which retain colorants by adsorption onto the matrix as well as by ion exchange, are unsuitable for the chromatographic examination of colorants according to their net molecular charge. With ion-exchange celluloses, matrix adsorption is minimised, especially if 8 M urea is used as a solvent. Accordingly, if colorants in 8 M urea solution buffered at pH 7.5 are passed over a column of DEAE cellulose (or preferably the quaternary derivative) in its chloride form, those with zero net charge are not adsorbed. The charged colorants which are adsorbed may be eluted in order of increasing net charge by a sodium chloride gradient. The effluent may be monitored automatically as in the case of gel permeation.

Distribution patterns of the type shown in figure 4 are obtained giving the relative proportions of molecules with different net negative charges (numbers of carboxyl groups). Results have been obtained with synthetic colorants and with a refinery brown liquor colorant. Again, the liquor colorant falls within the range of properties displayed by the synthetic colorants. The large proportion of unadsorbed (zero net charge) material in the lysine colorant is interesting, being a consequence of the Zwitterionic character of the molecule.

RESIN DECOLORISATION

The factor which has most influence on resin performance is the size of the colorant molecules relative to the pore size distribution of the resin, which decreases with increased cross-linking. The larger the molecule, the more its diffusion into the pores is restricted, and the lower the probability of its being adsorbed. This can be illustrated experimentally:

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[4] Laurent, T. C. and Killander, J. 1964. A theory of gel filtration and its experimental verification. J. Chromatog. 14: 317-322.

Dowex 1-X2 and 1-X10 (differing only in the degree of cross-linking, 1-X10 being the higher) are used to decolorise standard colorant solutions. The colorant effluent from the 1-X10 has the higher N-value; i.e., higher molecular weight colorant is rejected.

Retention of colorant is thought to take place by two mechanisms: ion-exchange, and adsorption onto the resin matrix. The more highly charged colorant molecules, being more strongly held by the ionic mechanism, can displace those with lower net charges. This is illustrated in the decolorisation of 2 week old glycine colorant on 401S (fig. 5). The lower molecular weight peak is due to displaced material of lower charge. This is confirmed by the net charge profiles of the influent and effluent colorants (fig. 6), where the effluent has a lower content of colorants with 3 and 4

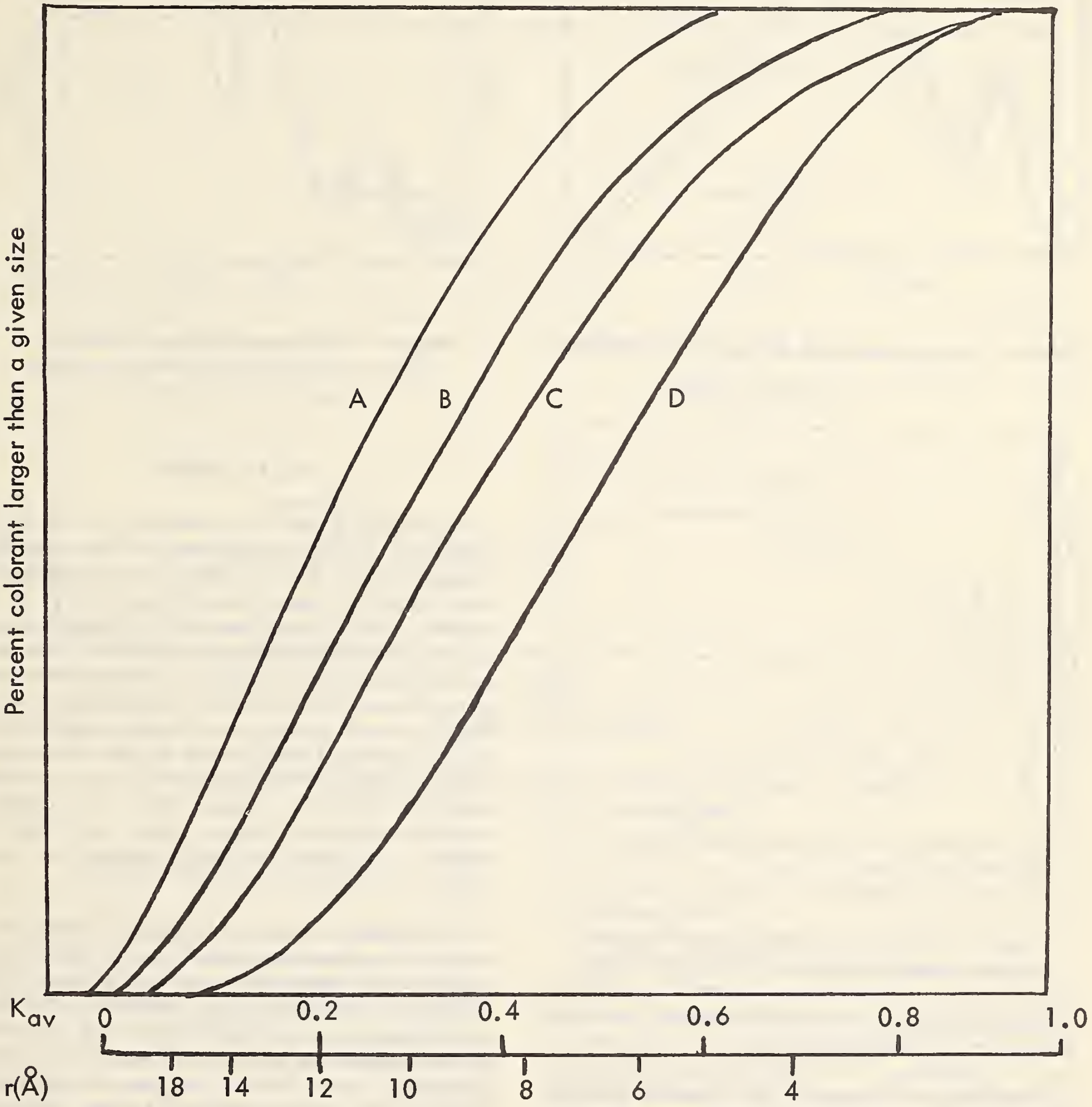

Figure 3. — Molecular size distribution of colorants. A: Lysine, B: Brown Liquor, C: glycine, D: glucose colorant.

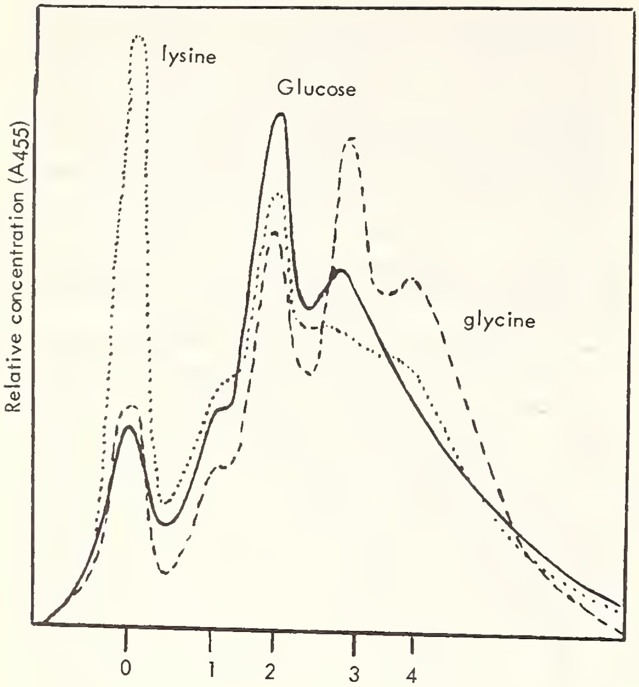

Figure 4. — Net anionic charge distribution of colorants.

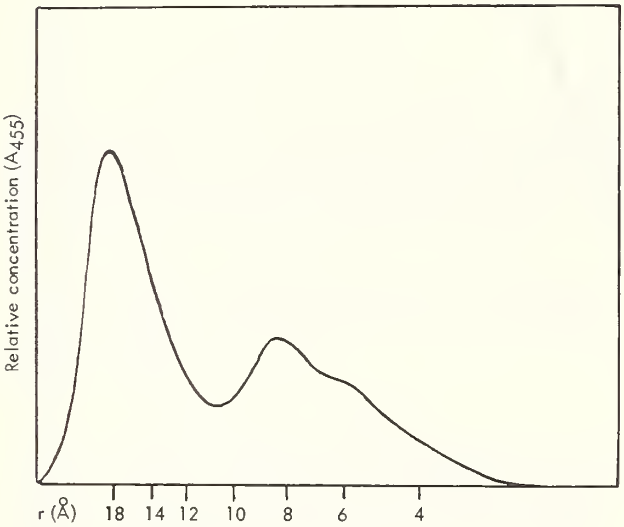

Figure 5. — Molecular size distribution of glycine colorant rejected by Amberlite IRA 401S resin.

charges and higher contents of 2 (displaced) and 5 and above (rejected on account of size).

Regeneration of resins with sodium chloride removes only the colorant which is ionically adsorbed. Adsorption by the matrix is attributed to Van der Waals forces and depends on the lipophilic nature of the colorant. This material is desorbed only on washing with alkali.

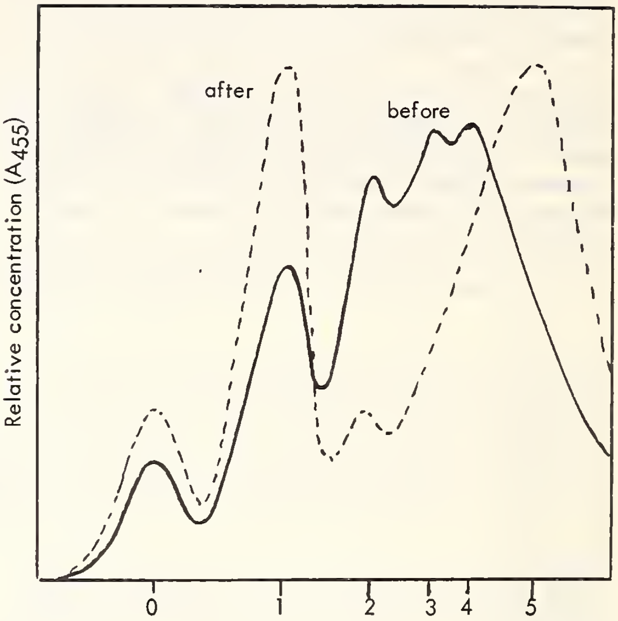

Figure 6. — Net anionic charge distribution of glycine colorant before and after treatment with IRA 401S resin.

SELECTIVITY

Assessment of resin performance by monitoring the effluent at a single wavelength can give misleading results, for rarely does the colour effluent coming off a resin have the same spectrum as that going on. Portions of the colorant have been selectively removed, each class of resin being most suited to the removal of one particular type of colorant. In the example quoted above, Dowex 1-X2 selectively removes high molecular weight colorant, giving a low molecular weight colorant in the effluent. Dowex 1-X10 exhibits the opposite behaviour due to the rejection of large molecules, which in the more porous resin have access to adsorption sites and, having a higher net charge, can displace the smaller colorant molecules of lower charge.

The logical outcome of this resin selectivity is to use two complementary resins in series, each removing the colorant type for which it performs most efficiently. Thus, Dowex 1-X2 followed by 1-X10 will give 97 percent decolorisation of 60 bed volumes of glycine colorant ($A_{455} = 5$) whereas the component resins give only 83 and 76 percent respectively. Similarly, the use of Amberlite XE 258 and Kastel A501D in series is more effective than either alone. The molecular size distribution of colorant retained or rejected by each resin is exactly complementary (fig. 7).

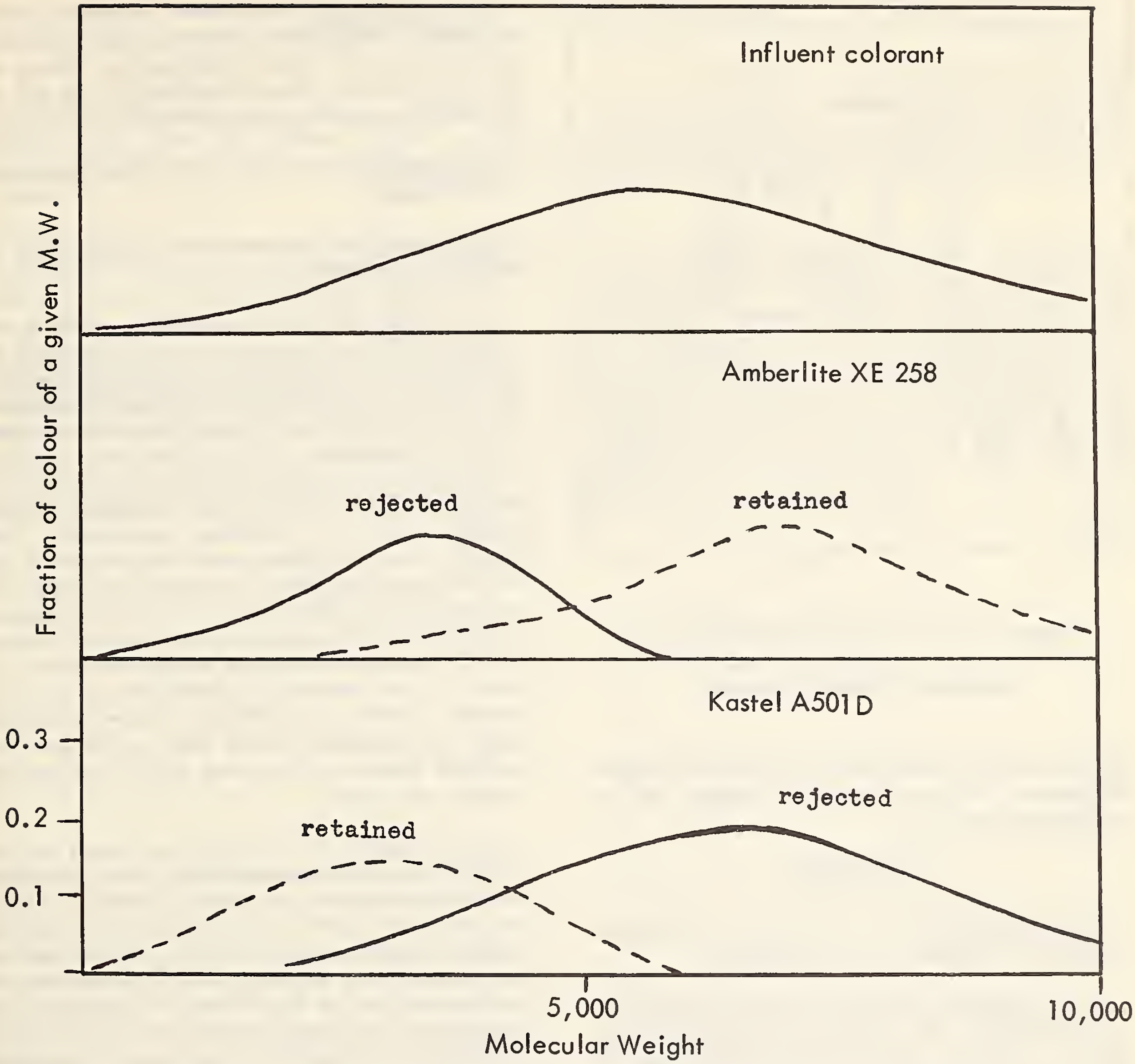

Figure 7. — Molecular weight (for linear molecules) distribution curves for colorant rejected or retained by the anion-exchange resin.

LIQUOR DECOLORISATION

A typical refinery liquor colorant composition could be represented to a first approximation by glycine colorant containing an additional 10 to 20 percent Zwitterionic material which, although effectively uncharged, is still highly polar and is retained neither by the ionic mechanism nor by the adsorption onto the relatively non-polar matrix of conventional polystyrene resins. The effluent colour from a liquor decolorised by 401S has a high proportion of this unchanged material (fig. 8). Lysine colorant (containing about 50 percent Zwitterionic material) is never more than 50 percent decolorised by conventional resins.

Thus, Zwitterionic colorants present a difficult problem in liquor decolorisation. Although their electrical neutrality makes them nonremovable by ion-exchange, they are retained normally at pH 9.5 (when the amino-groups are non-ionised), in the presence of formaldehyde (which combines with the amino groups to give the weakly basic methylolamine), or after deamination with nitrous acid. A suitably designed resin with a matrix having a high affinity for this material is needed. Resins with the more polar

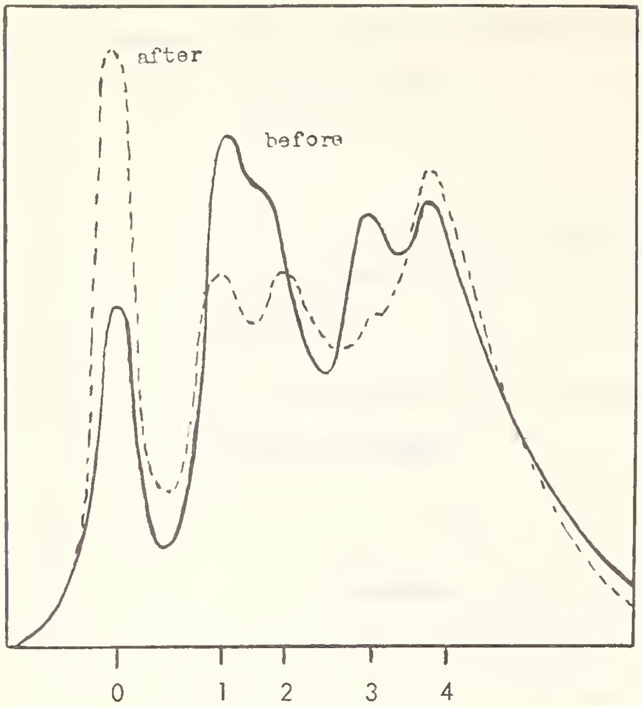

Figure 8. — Net anionic charge distribution of brown liquor colorant before and after treatment with IRA 401S resin.

phenolic matrix, while generally poor in decolorisation performance, do show signs of affinity for the Zwitterionic colorants.

DISCUSSION

E. NABORNEY: What were the experimental conditions for determining this net charge?

E. C. MULLER: The column used consisted of 10 ml. of Whatman DE32, which is a diethylaminoethyl cellulose. The flow rate was about half a ml. per minute, and the sodium chloride gradient was from zero to 0.5 M over 300 ml.

A. VanHOOK: You mentioned that these various molecular size parameters could be translated into effective molecular weights in ordinary dimensions. How was this done?

E. C. MULLER: To make the conversion from relative size to actual molecular weight, it is necessary to assume shapes of the molecules.

A. VanHOOK: How were the infrared spectra obtained?

E. C. MULLER: They were recorded on a Perkin-Elmer 457 spectrophotometer; the potassium bromide disks were 2 mg. of substance in 200 mg. of KBr. The solution spectra were on 30 mg./ml. of chloroform, measured in an 0.2 mm. cell.

C. C. CHOU: Do you use a ratio of absorbance at two wavelengths?

E. C. MULLER: Yes, the ratio of the absorbance at 455 nm. to that at 520.

C. C. CHOU: I am interested in the meaning of the N value. The idea of relating the ratio of absorbance at high and low wavelength to the degree of conjugation and, to some extent, to molecular weight of colorants is in the right direction. However, I have some doubts about the applicability of the N value as an indication of the molecular weight, if the ratio of absorbances at 520 and 455 nm. is used for the calculation. As you probably know, in ultraviolet spectroscopy, the addition of one conjugated bond into a compound can shift the absorption peak by as much as twenty nm. Accordingly, the addition of two or three conjugated bonds could shift the absorption from 455 to 520 nm., but the increase in molecular weight would be only about 75. For instance, if a molecular weight of a colorant is 5000, upon addition of three conjugated bonds, the absorption would shift to 520 and the molecular weight would be only 5075. Therefore the change is very little.

E. C. MULLER: Dr. Parker did not actually use the N value to measure molecular weight. All he attempted to show is that there is a correlation between N values and molecular weights — that on the whole, as the molecular weight goes up, so the N value will also go up. He would not go so far as to try and measure molecular weights by this method. The derivation of this equation and the relationship of n and N has been described by Dr. Parker in a paper read at a previous Technical Session[5]. But it's only an indication of molecular weight, and is not intended to be a measure of it.

C. C. CHOU: I think the removal of the Zwitterionic colorant depends on the nature of the colorant. Sometimes you can shift the net charge by changing the pH.

E. C. MULLER: Do you mean the net charge within the molecule?

C. C. CHOU: Yes, you said that there is no net charge in this particular colorant, but I think that, in some cases, you may be able to put on a charge by adjusting the pH — as with proteins or amino acids.

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[5] Parker, K. J. and Williams, J. C. 1969. The isolation and properties of sugar colorants Proc. 1968 Tech. Sess. Cane Sugar Refin. Res. 117-128.

E. C. MULLER: Yes, I'm sure that's very interesting, because by being able to do this, you might, in fact, affect and improve the color removal since, to a large extent, color removal depends on the presence of a net charge.

C. C. CHOU: You seemed to imply that since the Zwitterionic color has no net charge, it cannot be removed by commercially available resins. If you change the net charge, it may be removable.

E. C. MULLER: Yes, you may well be right. I think this would be a very interesting improvement in the use of these materials.

W. W. BINKLEY: I would like to know how the numbers were obtained in the ionic charge, on the abscissa in figure 4. For example, how did you decide it was 2?

E. C. MULLER: It was done simply by finding peaks in those widely separated positions. The peaks do come in definite steps, and it seems reasonable to assume that they would correspond to a small integer. However, this has not yet been confirmed.

F. G. CARPENTER: I think that we should all congratulate Dr. Parker on doing a fine job. He has drawn what I consider excellent conclusions from work with ion exchange, but we must remember that he is basing everything on ion exchange resins and the properties of colorant on ion exchange. He has never really separated the colorants into individual constituents. He has groups, and it is masterful interpretation of data to find so much about the colorant while it is still mixed up.

THE RATE OF REACTION OF SYNTHETIC COLORANTS AND RESINOUS ADSORBENTS

by

James E. Rader and Robert E. Anderson
Diamond Shamrock Chemical Company
Redwood City, Calif.

(Presented by Robert E. Anderson)

ABSTRACT

Three types of colorants were prepared. Each of these was contacted with several different resinous adsorbents and the rate of uptake determined. The rates are seen to be dependent on both the nature of the colorant and the structure of the adsorbent. Some generalizations can be drawn from the data as to expected column behavior.

INTRODUCTION

Some months ago we initiated a research project on the decolorization of sugar solutions with resinous adsorbents in a laboratory remote from a sugar refinery. In reviewing the literature concerning the nature of the color bodies, we found that the subject remains extremely complex. While some fine and increasingly sophisticated work is presented each year, there is still no general agreement even on how the colorants should be classified. Older classifications such as caramel, melanoidin, polyphenol-iron complexes, etc., have been supplemented with such classifications as anionic, weakly basic amphoteric and strongly basic amphoteric.

The approach found most useful was that of N. R. Smith[1]. After studying the color bodies present in sugar by a variety of techniques, he synthesized model colorants and correlated these with naturally occurring colorants. These model colorants gave a practical and logical place to start.

The three model colorants, caramelized sucrose, melanoidins, and alkaline degraded fructose (ADF), have a gradation in both molecular weight and ionic character. This is shown, grossly simplified, in table 1. Working with these models, we hoped to be able to see some logical relationship between the properties of the model colorants and the way in which they interact with particular resinous adsorbents.

Table 1. — Synthetic colorants used

Colorant	Source	Estimated M. W. range
Alkaline degraded fructose	Fructose + NaOH	500
Caramel	Sucrose + heat	500 to 1,000
Melanoidin	Glucose, sucrose + amino acids	? to 50,000

Order of decreasing ionic character:

ADF > Melanoidin > Caramel

Resinous adsorbents also come with a gradation of properties. The four chosen for the initial work differ markedly in ionic functionality and physical structure (table 2). These were:

1) Duolite ES-111, a crosslinked polystyrene based ion exchange resin containing quaternary ammonium functionality. Such a resin is highly ionized at all pH values and a large part of its decolorizing ability is due to true ion exchange. This is the type of resin widely used for chloride cycle polishing of liquid sugars.

2) Duolite S-37, a phenol formaldehyde condensate containing a mixture of secondary and tertiary amine groups. The polymer structure is porous but relatively rigid. This adsorbent is gaining wide acceptance for the removal of trace organic colorants in surface waters because of the ease with which it can be regenerated.

3) Duolite ES-33, a phenol formaldehyde condensate containing tertiary amine groups. It also differs from Duolite S-37 in having a much more flexible structure which can readily accommodate even larger molecules.

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[1] Smith, N. R. 1967. Fractionation of sugar colorants with molecular sieves. Proc. 1966 Tech. Sess. Cane Sugar Refin. Res. 84-102.

Table 2. — Resinous adsorbents used

Trade name	Matrix[2]	Functional group	Physical group	Capacity to HCl Eq/L	Typical moisture retention
Duolite S-30	P-F	Phenolic hydroxyl	Granules	-	48
Duolite ES-33	P-F	Tertiary amine	Granules	0.7	58
Duolite S-37	P-F	Secondary and tertiary amine	Granules	2.3	55
Duolite ES-111	PS	Quaternary ammonium	Beads	1.0	67

[2] P-F = Phenol-formaldehyde condensate.
PS = Crosslinked polystyrene.

4) Duolite S-30, a phenol formaldehyde condensate whose hydrophilicity is due solely to the oxygen-containing groups in the polymer. It also has a porous but rigid structure. It has found wide use as a heavy-duty, reversible adsorbent for over 20 years.

EXPERIMENTAL

The colorants were prepared as concentrated reagents following the recipes given by Smith[1]. The solutions were filtered through an extra-fine glass frit to remove solids. Color measurements were made at 420 nm. using a Beckman DU spectrophotometer. All solutions were adjusted to pH 7 before being measured. The solutions used in the decolorization experiments were made by dissolving a given amount of colorant in 50 Brix sucrose. Each of the resinous adsorbents was cycled several times with dilute sodium hydroxide and sodium chloride to remove any residual color from the manufacturing process. They were then rinsed with deionized water, filtered and bottled until use.

Measurements were made by weighing a given amount of adsorbent into a series of small screw-top jars and adding a given amount of colored sucrose solution. After the jars had been shaken for a given period of time, the resin was allowed to settle, and the color remaining in the supernatant was determined and compared with that of the untreated solution.

In the preliminary experiments, we found that each of the four adsorbents removed any of the three colorants, if the ratio of resin to solution were high enough and enough time were allowed. These loading curves were all very similar if at least 24 hours were allowed for the contact. Actually, in each case a ratio of 5 g. of resin to 50 ml. of solution gave at least 95 percent removal.

A more meaningful line of investigation was the measurement of the relative rate of adsorption with the various combinations. Using the ratio of 5 g. of resin to 50 ml. of solution, the contacts were run for times varying from 5 to 120 minutes. The solutions were filtered and the remaining color determined. This gave a series of adsorption rate curves.

Rate curves. — Let us look first at how the three synthetic colorants respond to a given adsorbent. The quaternary ammonium resin, Duolite ES-111, shows a very rapid uptake of the alkaline degraded fructose (ADF) (fig. 1), and a high capacity for it. The ADF has a moderate molecular weight and is highly ionic. It can be assumed that its pickup is largely through a true ion-exchange mechanism with a high driving force. Notice that the pickup is over 90 percent complete in less than 15 minutes.

This adsorbent shows considerable less capacity for the other two colorants in the 2 hr. allowed. Even here, though, there is an interesting difference. The pickup of the melanoidins is quite rapid initially with over 50 percent removal obtained in the first 15 minutes. While the pickup of the caramel and the melanoidins is essentially the same after 40 minutes, the initial rate with the caramel is appreciably slower. The caramel has little ionic character. The high initial rate with the melanoidin may be ascribed to the presence of a fraction of relatively low molecular weight components with ionic functionality.

The response of the highly porous tertiary amine adsorbent, Duolite ES-33, to the three colorants is quite different than that of Duolite ES-111 (fig. 2). This adsorbent shows an excellent pickup of both the caramel and the ADF and a good pickup of the melanoidins. It is apparent that the high porosity of the adsorbent allows it to accommodate a very

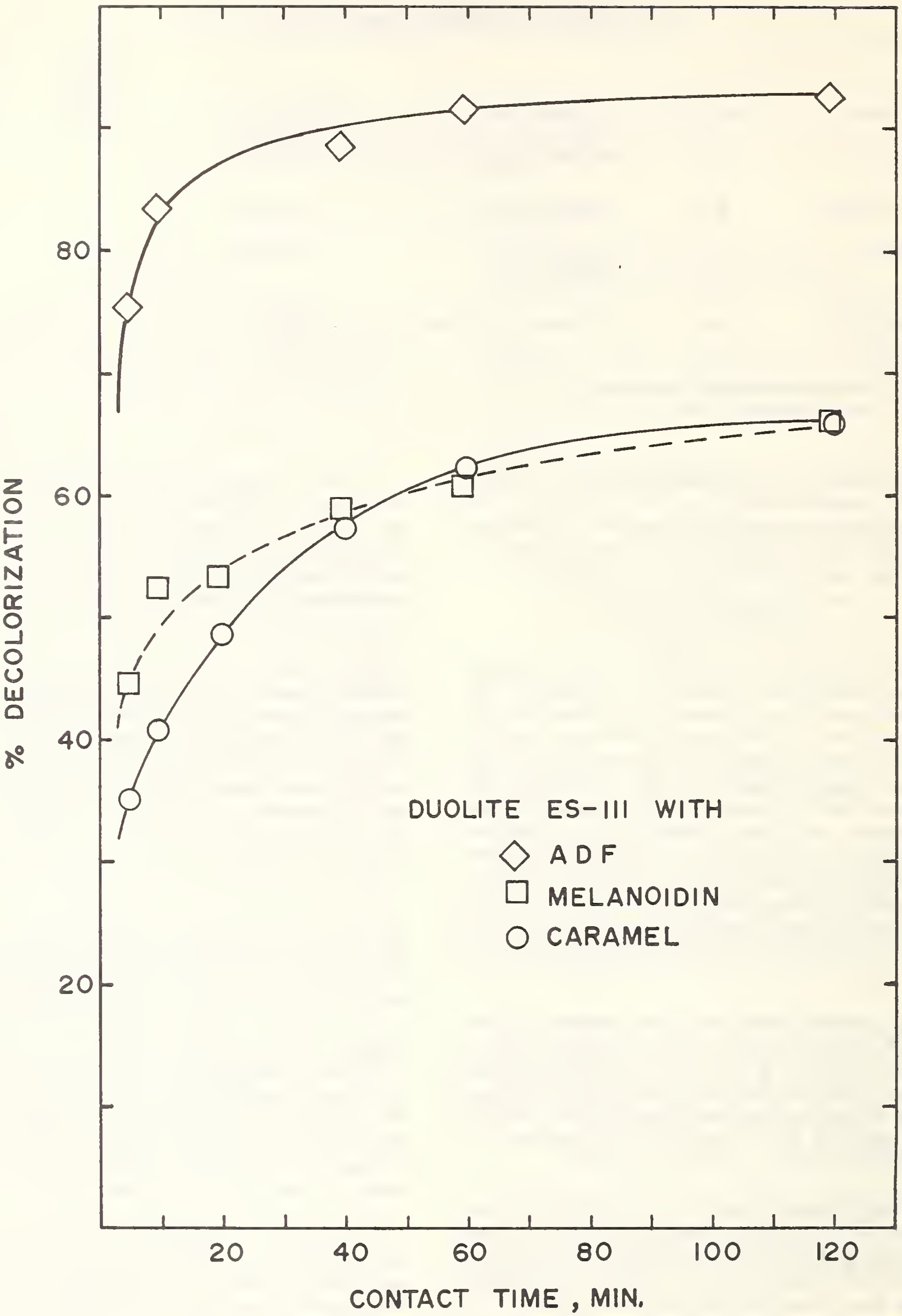

Figure 1. — Colorant adsorption curves for Duolite ES-111.

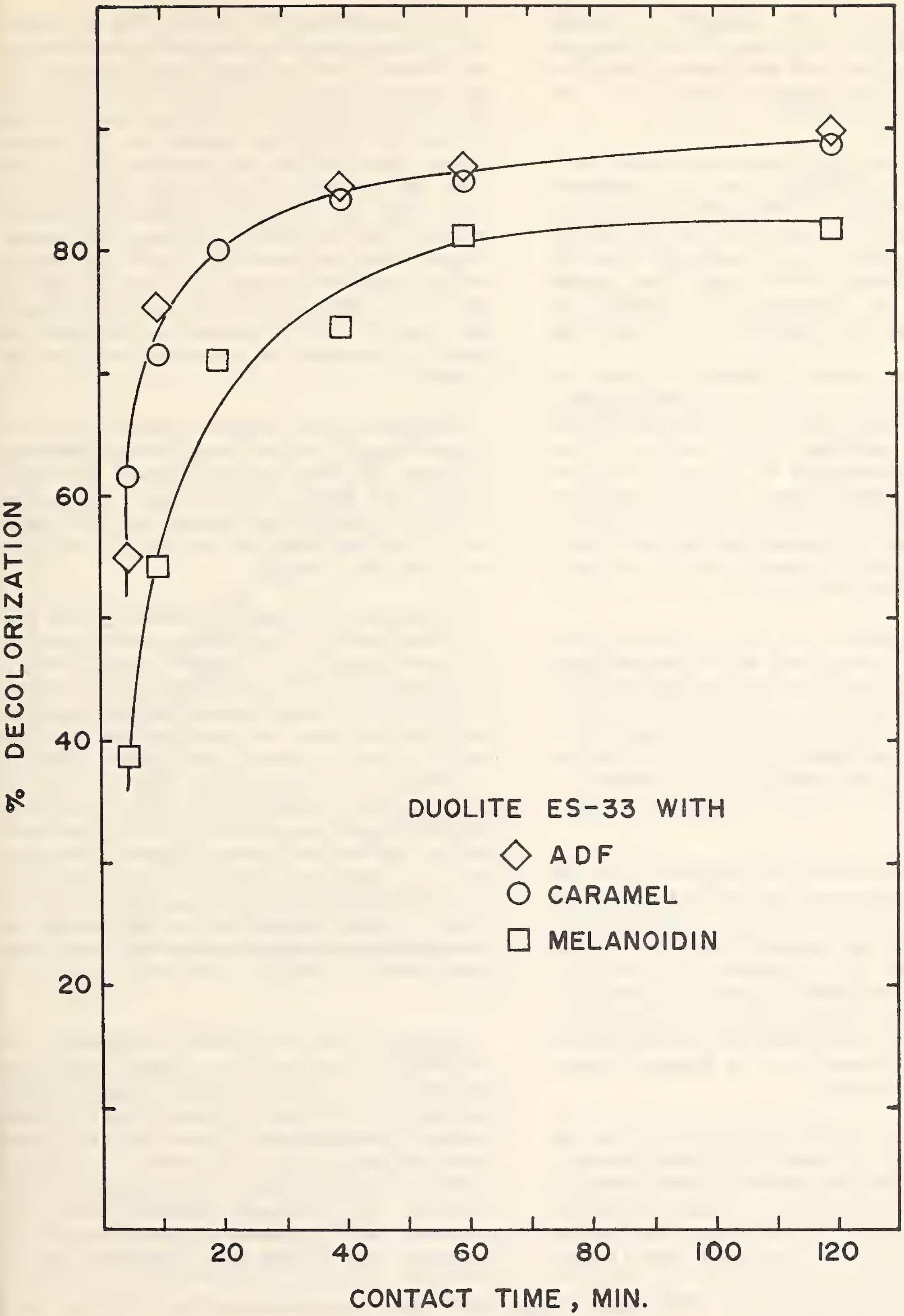

Figure 2. — Colorant, adsorption curves for Duolite ES-33.

appreciable fraction of the melanoidin components relatively rapidly. However, none of the components show quite the same rapid initial pickup observed in the first case. This probably indicates that ionic interactions are less important in this case.

Duolite S-37 would be expected to act much as the Duolite ES-33 as to the effect of the ionic interactions. However, it should show the effect of its higher rigidity. The ADF and caramel show similar behavior: an appreciable capacity, but attained rather slowly (fig. 3). The melanoidins show a rapid initial uptake, probably due to components of relatively low molecular weight, and a rather slow increase after that.

The non ionic adsorbent, Duolite S-30, shows only a modest capacity for any of three colorants within the 2 hr. time allowed (fig. 4). The low pickup of the ADF can be attributed to the absence of ionic interactions. The adsorption in this case is due to Van der Waals and similar forces, where the molecular weight of the component being adsorbed becomes an important factor. The melanoidins might well show a better pickup than the caramel, except for the rather rigid structure of the Duolite S-30.

The marked difference in the way that the various pairs can react is emphasized by how three different adsorbents behave with ADF and caramel. With ADF the quaternary ammonium resin, Duolite ES-111, gives an excellent decolorization, even better than that of the highly porous Duolite ES-33 (fig. 5). However, with the caramel, the Duolite ES-111 is essentially no more effective than the non-ionic Duolite S-30 (fig. 6).

In the discussion above, the emphasis was on the amount of decolorization obtained in the initial 15 min. or so of contact. Remember, however, that in each case there was supposedly enough adsorbent present to remove 90 to 95 percent of the color in 24 hours. The apparent capacity of each of the adsorbents in the two hours allowed is really a measurement of the rate of the reaction. Notice how this rate falls off as the polarity and porosity of the adsorbent decrease through the series used.

Extrapolation to column performance. — What do these results mean in terms of processing solutions? According to Zievers and Novotny, standard practice in decolorization of cane liquors with resins is a flow rate of 1 to 2 g.p.m./sq.ft.[3]. Assuming a bed depth of five feet, a flow rate of 1 g.p.m./sq.ft. gives a contact time of approximately 15 minutes. That is, colorant entering the top of the column will be in contact with the adsorbent about 15 minutes, during which time it will either be picked up or will pass out the bottom of the column. The amount of color that comes out the bottom of the column depends on a dynamic process — how fast can the adsorbent pick up the color — not on how much can it pick up. These rate curves show why the porous quaternay ammonium resins have been successful in decolorizing cane liquors. They are used to polish liquors that have already received considerable refining. The colorants left are likely to be relatively low molecular weight species that were not readily removed by adsorption on carbon, or derivatives of invert sugar formed in the processing.

Decolorization with resinous adsorbents is not a surface adsorption process. These resinous adsorbents are active for color pickup throughout their total volume, just as they are for ion exchange. The problem is to get the colorant into the resin, and as we saw in some of the rate curves, this may require more than the 15 min. often allotted.

The activity of the bulk of the resin particle and the implications of this on rates is brought out nicely in a recent paper by D. F. Bagster[4]. Using a refinery syrup and Deacidite FFIP screened to three different size ranges, he ran batch contacts somewhat similar to those described above. He found that while the fine particles had a much faster initial rate of decolorization, at equilibrium all three sizes showed the same degree of decolorization. Further, the initial rates were roughly proportional to the relative surface areas for the three size fractions. Actually, this is the same as saying that the rates were inversely proportional to the square of the practice radii. This is a very common relationship in the kinetics of conventional ion exchange where the slow step in the overall process is diffusion of the solute in the resin phase.

Desorption. — To be practical economically, an adsorption process must be reversible unless the adsorbents are very inexpensive, and resinous adsorbents are not. Thus, this paper would be more valuable if rates of desorption had also been run. These would have been found to be dependent on the type of adsorbent and the nature of the colorant, just as in adsorption. The quaternary ammonium resins are notoriously hard to regenerate. Bagster found that if the highly loaded resins were equilibrated with a

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[3] Zievers, J. F., and Novotny, C. J. 1969. Review of sugar oriented ion exchange practices. Proc. 1968 Tech. Sess. Cane Sugar Refining Res. 35-50.

[4] Bagster, D. F. 1970. Batch decolorization of sugar liquor with ion exchange resin. Internatl. Sugar Jour. 72: 200-203.

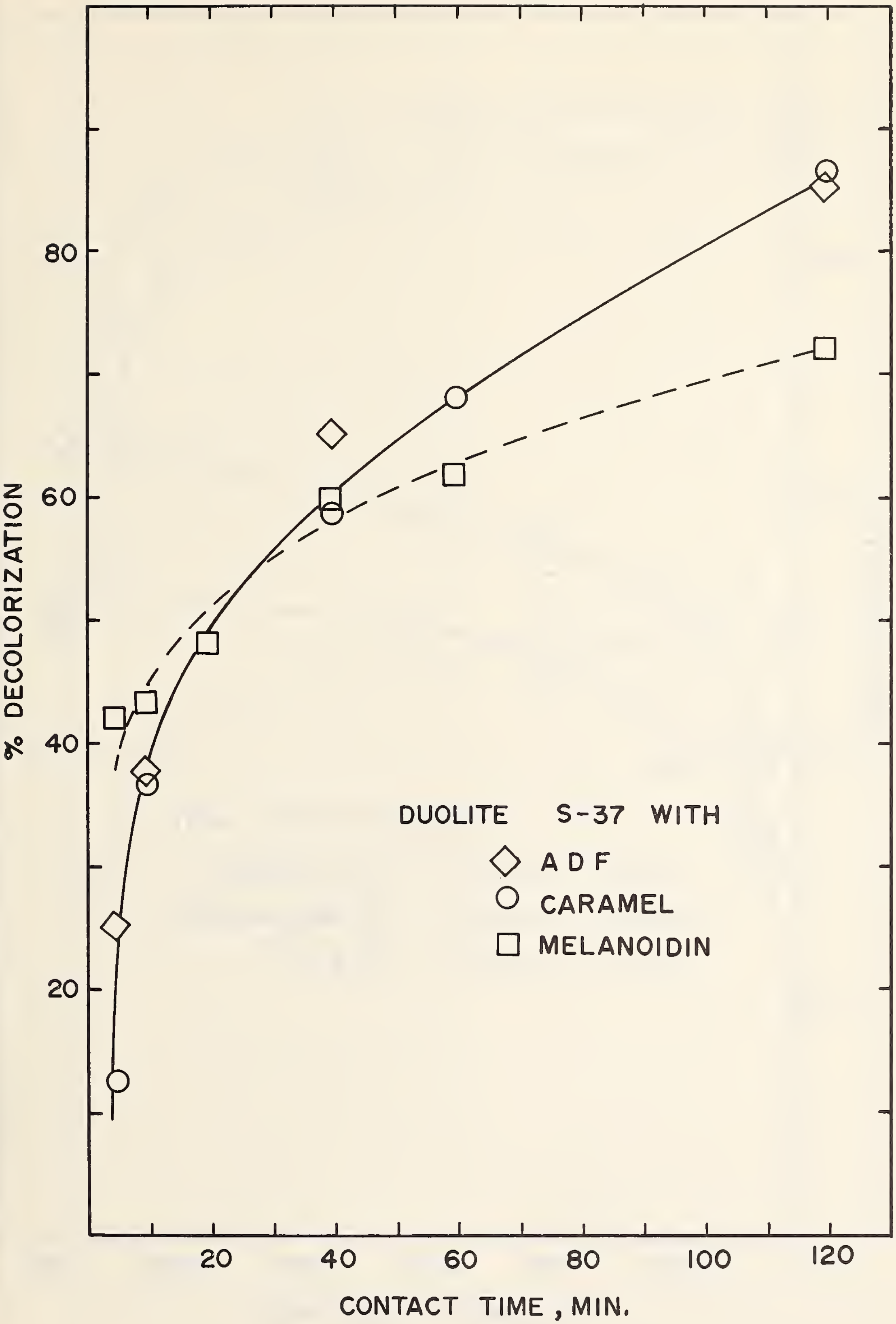

Figure 3. — Colorant adsorption curves for Duolite S-37.

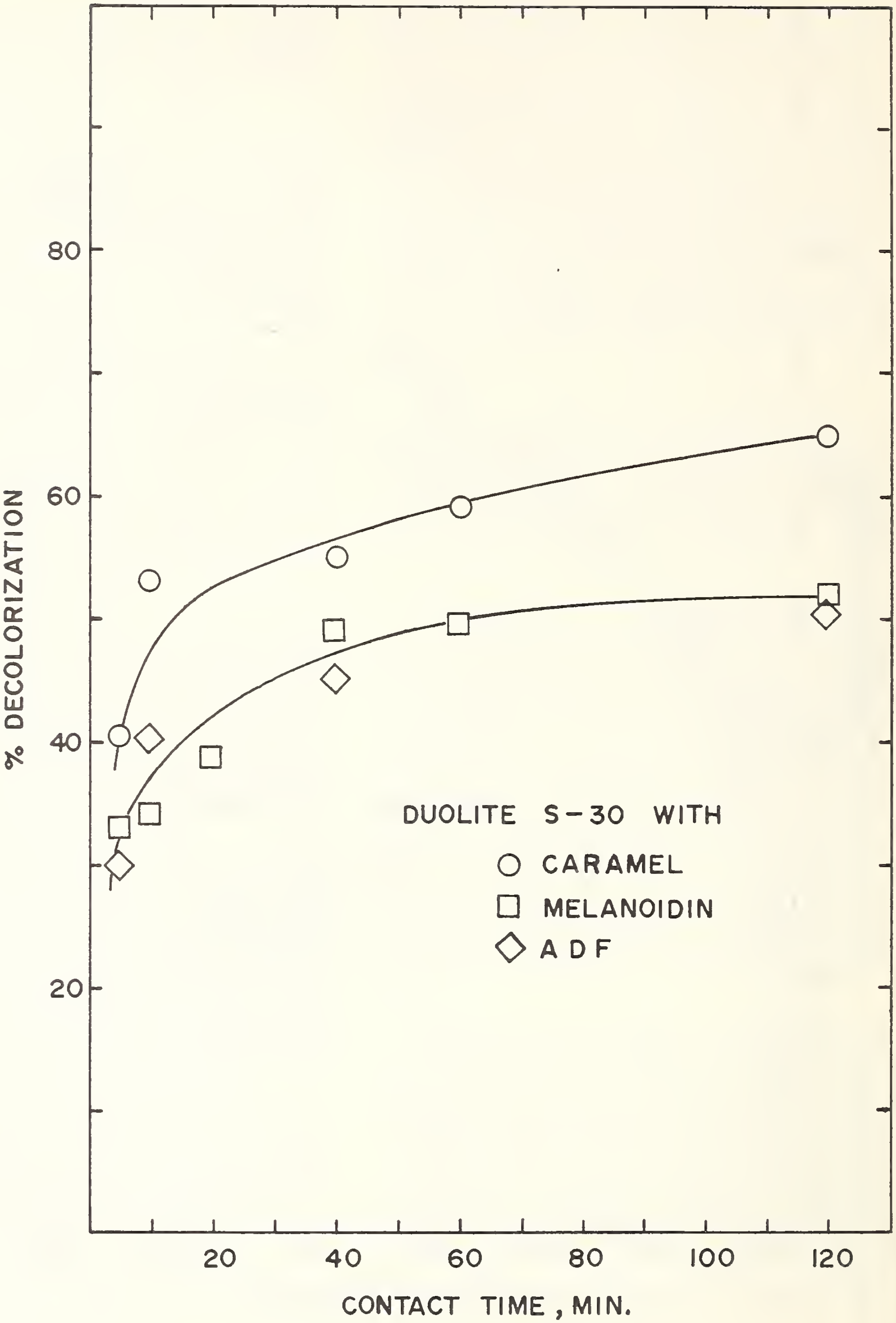

Figure 4. — Colorant adsorption curves for Duolite S-30.

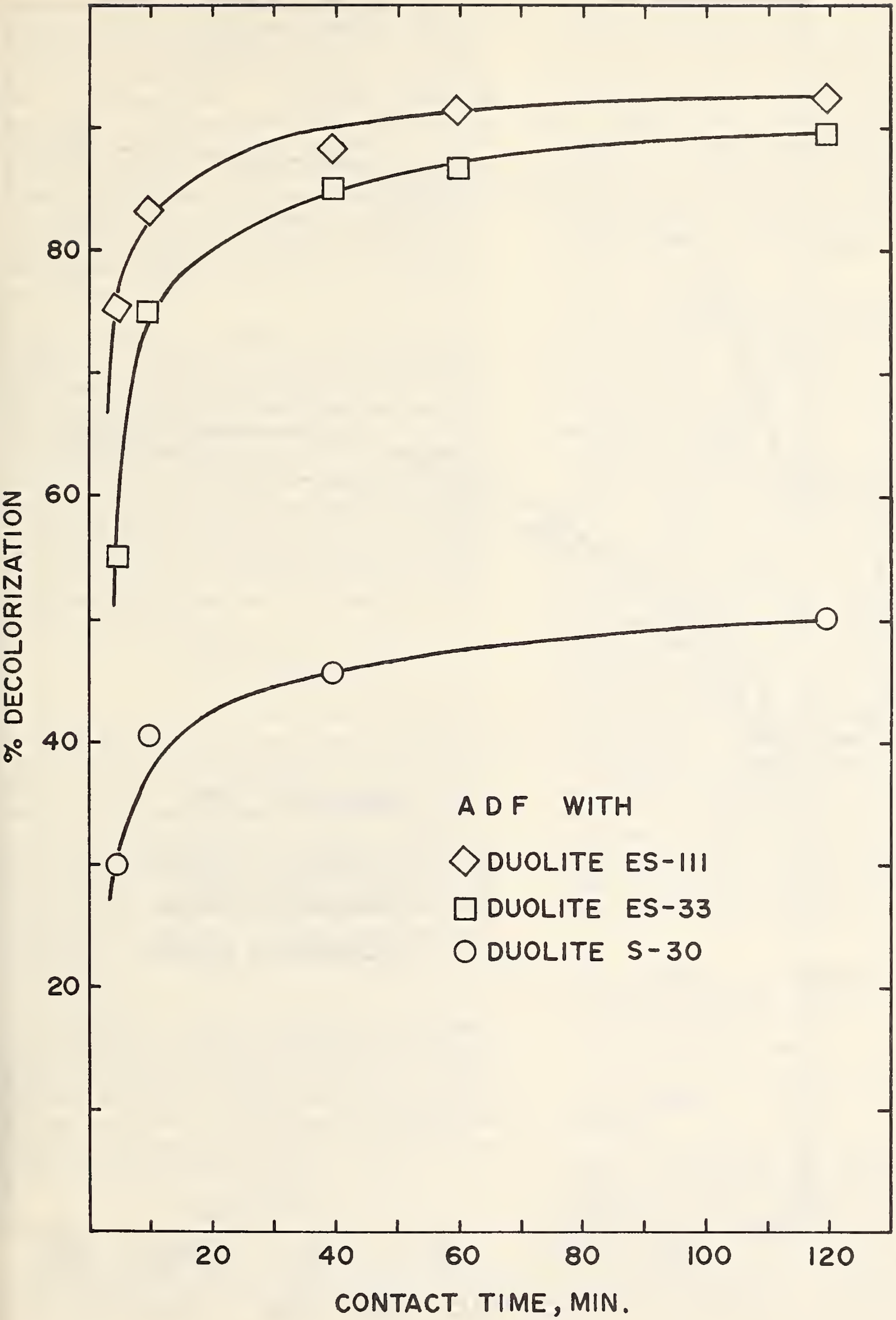

Figure 5. — Adsorption of alkaline degraded fructose by different adsorbents.

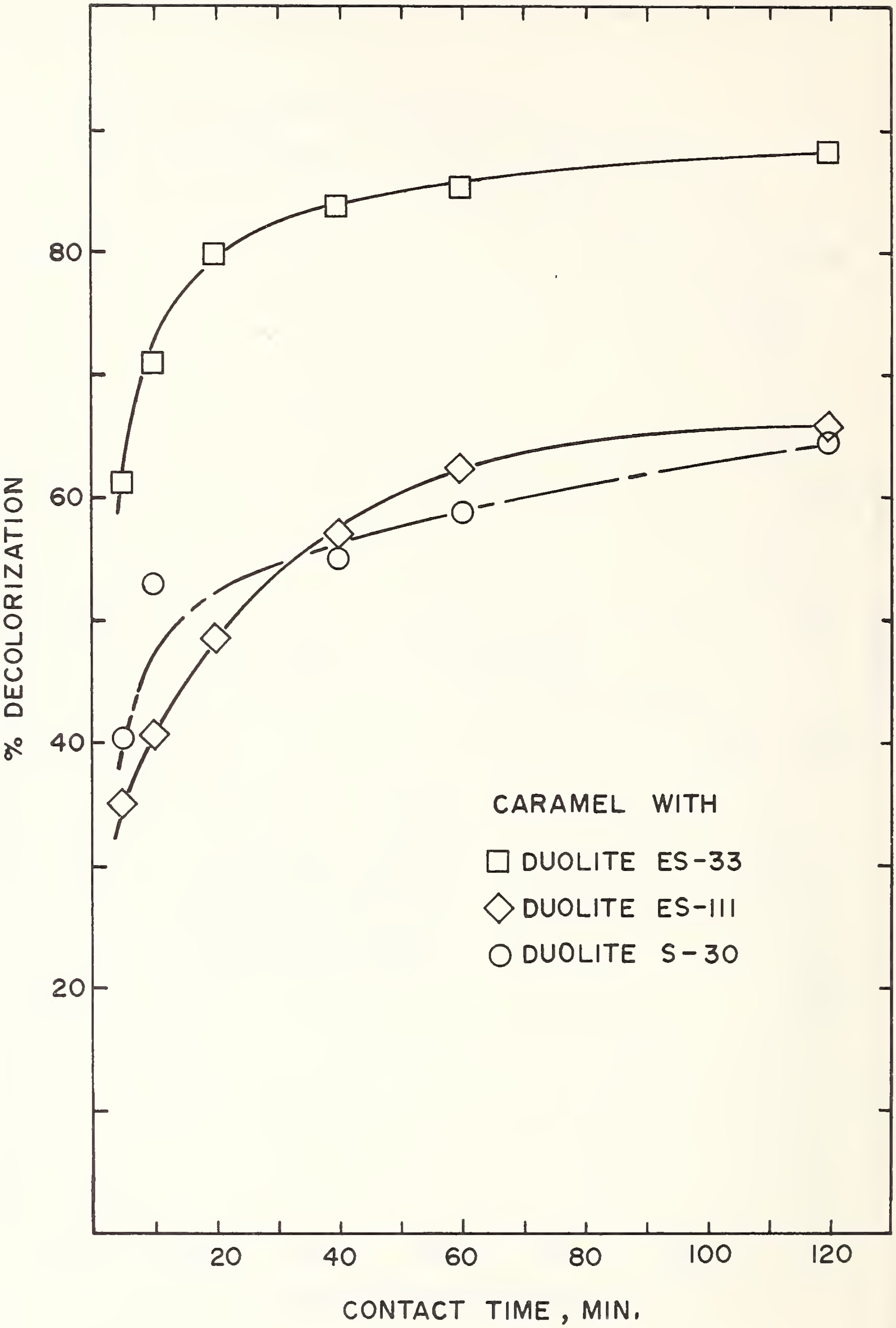

Figure 6. — Adsorption of caramel by different adsorbents.

colorless sugar solution, there was essentially no transfer of color to the solution phase[4]. This again indicates that the adsorption process in this case is largely ion exchange, with a high degree of selectivity for the colorant ion. A reasonable degree of regeneration is obtained with strong salt solutions. However, even this is not completely effective. Schneider and others[5] showed that this type of resin tends to pick up the colorant as a concentrated band in the outer one-third to one-half of the radius of the bead. When the resin is regenerated with salt, part of the colorant is displaced and part of it is smeared on into the resin particle.

The weakly basic adsorbents do not form well defined ionic bonds with the colorants. Raising the pH of the system readily displaces the adsorbed material. This is accomplished by washing the adsorbent with dilute caustic or ammonium hydroxide. The latter may be particularly attractive as it can be recovered by liming the waste, or it may be combined with other waste streams and converted to animal feed. This ready reversibility of the weak base adsorbents mades them ideal scavengers ahead of the quaternary ammonium type. They will remove the bulk of the high molecular weight constituents that tend to exchange irreversibly on the more polar resins.

CONCLUSION

Much of the past work on ion exchange decolorization in the cane sugar industry has concentrated on the quaternary ammonium resins. Where a variety of resins has been tried, there have tended to be minor variations of this basic structure, such as varying amounts or types of crosslinkage, or resins from various manufacturers that are more alike than different. Judging from the literature, the European and Japanese sugar industries have both made more use of resins of varying properties to do a progressive decolorization than has been done in the United States.

In conclusion, we wish to emphasize that adsorption and desorption are dynamic processes. The range of colorants occurring in sugar processes is very complex. The best answer to removing these components will not be found with a single material. In finding good answers, each system will have to be evaluated in terms of both rate and ultimate capacity.

DISCUSSION

J. R. NICHOLS: The work you report is on single colorants; what might these plots look like if you used mixed colorants?

R. E. ANDERSON: There was one experiment in which we mixed all three of the colorants together. None of the adsorbents showed any better behavior with a mixture than the poorest behavior exhibited with any single colorant. This has been mentioned in the literature before, as an admonition that if adsorbents are used, they shouldn't be mixed. That work is a little different from this, but if different adsorbents are used to take out different colors, they should be used in series. For any particular colorant, there is probably one particular type of adsorbent that will work better than any other.

F. G. CARPENTER: I would like to add to that thought. I think the biggest problem of the whole sugar industry is our doubletalk when we speak of color. We all recognize that the colorant in sugar is most definitely a mixture. Ken Parker just showed us that he has a mixture of many anionic colorants. This afternoon Dr. Farber is going to name about a dozen of the cane pigments in that mixture. But we still measure colorant as though it were a single term. We use a -logT at 420 and say that's the color. That's the sum of all this infinitude of colorants. The results for the mixture were no better than the worst with any single colorant and that's just exactly what you would have expected. In fact, even in your so-called single colorants, you still had a mixture of many, and so you're still not quite on the trail. You're aimed at it — you've separated the color into three parts. What we'd like to do is to separate it into 30 or 300. Then we could really get down to what was going on. It is my feeling that the whole industry will not progress much farther until we can really measure these things one at a time and find out which ion exchanger is doing what to individual colorants, one at a time. This just emphasizes the point that when you have a mixture you've got a mess that you really can't quite resolve. It's what the statisticians call "confounded."

P. F. MEADS: Do I understand that these are in 50° Brix sugar solutions?

R. E. ANDERSON: Yes

P. F. MEADS: You didn't vary the concentration of sucrose?

R. E. ANDERSON: We ran some preliminary experiments in which it appeared, at least as a first approximation, that whether we ran these with or without sucrose — 0 or 50 Brix — there was a very minor difference in the rate of exchange. This was only an approximation — we were rather surprised at the result — but this was our observation.

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[5] Schneider, F., Schliphake, D., and Paleos, J. 1968. Zucker. 21: 268.

P. F. MEADS: You conclusion then is that the rate is independent of the sucrose concentration?

R. E. ANDERSON: Yes.

J. F. DOWLING: The relationship of rate of exchange of the color bodies is independent of sucrose, but is it independent of the ash? If we have a high sodium content, are we to assume that the resin is going to take preference for the sodium and kick the color out?

R. E. ANDERSON: With a quaternary resin, definintely not, because there is a very selective exchange. If you are trying to take colorants out of a strong brine, that might be something else, but the normal ash content in sugar solutions is very minor. With the non-ionic or weakly ionic adsorbents, I don't think that salts will play any appreciable part in decolorization. They're going to be essentially inert.

F. G. CARPENTER: Isn't the amount of colorant in there minor too, in actual practice?

R. E. ANDERSON: Yes. We worried a little bit about the concentration of our colorant in these solutions. We really had no way of knowing, because even though you make these colorants up — receipes call for making up 20 percent solids solutions — I don't know whether one tenth of a percent or ten percent of those solids form colorants. So, we know we're working with relatively concentrated colorant solutions here, but I have really no idea what concentration.

F. G. CARPENTER: Did you try to measure the rates at different concentrations of colorant?

R. E. ANDERSON: No.

F. G. CARPENTER: You were working with black liquor, whereas in refinery practice they don't decolorize black liquor.

R. E. ANDERSON: That's right.

F. BRUDER: You had an equilibrium where you came to about 95 percent removal on one color — regardless of which color it is. Would you expect in a column operation that this equilibrium could be offset by the fact that you're going on with a lower concentration at each step, that is, as you go down the column. You have a time factor in your work, but you don't have the depth factor which actually comes into play when you're operating a plant.

R. E. ANDERSON: The length of time you can run a column really depends on what leakage you are willing to tolerate at the bottom of it. So you can load the adsorbents as high as you want to load them, if you don't care what comes out the bottom.

F. BRUDER: Of course, in the sugar industry we want everything out.

R. E. ANDERSON: If you are willing to put ten columns in a row and run through the series, you can load that first column completely. Then, when that goes, you take it off stream and put another fresh one down at the end, and you regenerate the first one. In practice, you couldn't do this because you couldn't stand the pressure drop, obviously. But how high you load the column depends on what leakage you are willing to accept and on how slowly you're going to run them.

F. BRUDER: The rate is an important factor, then.

R. E. ANDERSON: Right, it's rate dependent, as is any adsorption process.

F. G. CARPENTER: Would you care to comment on the rates on resin compared to the rates on carbons?

R. E. ANDERSON: If we look at practice in the sugar industry, I think the answer is fairly clear. We talk about 1 to 2 gallons per square foot on resins, whereas on bone char it's some very slow rate, volumewise. Rates with charcoal are also relatively slow. I think our rates are faster here, but the rates we're used to in ion exchange are the rates with quaternary resins. If you're going to use these nonpolar or less polar resins, you're going to have to go to slower rates to get really good performance. Although I think that even in these cases resins are much faster than charcoal.

F. M. CHAPMAN: About 20 times faster.

R. E. ANDERSON: It's going to depend on the resin system.

ION EXCLUSION – AN OVERLOOKED ALLY

by

James F. Zievers, C. J. Novotny, and E. A. Selvick
Industrial Filter and Pump Mfg. Co.
Cicero, Ill.

(Presented by C. J. Novotny)

ABSTRACT

Ion exclusion is applicable to partial purification of low purity syrups. With molasses, it produces a colored invert syrup at very low cost.

THEORETICAL BACKGROUND FOR ION EXCLUSION

Ion exclusion, as originally conceived(8), separates ionic from non-ionic solutes. This is still its primary use today, although the technique has been applied to separation of non-ionic solute mixtures as well (6). Ionic substances, because of the Donnan membrane exclusion effect, are repelled by the charges immobilized in an ion exchange resin. Non-electrolytes migrate into and out of the bead freely. This results in much greater concentration of ionic substances in the interstitial liquid than in the liquid within the resin beads.

When a column of ion exchange resin is fed an ionic and non-ionic solute mixture, the non-ionic portion is retained in the resin beads while the ionic salts are excluded and reach the effluent point first. The non-ionized solutes can then be washed out of the column with water and collected. There is, of course, an overlapping of the two fractions. This overlap mixture can be reworked, along with new feed, in a recycling step (7).

For separation of ionic from non-ionic substances by ion exclusion, the following general requirements for ionization constant, K, have been made by Wheaton and Bauman, (8):

Ionic Fraction	$K > 5 \times 10^{-2}$	Required
	$K > 2 \times 10^{-1}$	Preferred
Non-Ionic Fraction	$K < 2 \times 10^{-1}$	Required
	$K < 5 \times 10^{-2}$	Preferred

The volume of feed to be separated in the column is theoretically limited in that it must be less than the liquid volume within the resin beads.

Separations of non-ionic solute mixtures can be carried out with this method, too. Some molecules have affinities for the resin bead voids, while others prefer the interstitial voids. Depending upon the amount of crosslinking in the resin (i.e., percent divinylbenzene) the separation of large and small molecules can be obtained.

RESIN DESCRIPTION

The resin used was DOWEX 50W-X4 50 to 100 mesh. It is a strongly acidic cation exchange resin. The copolymerization of styrene with divinylbenzene (4 percent) results in a crosslinked or three-dimensional polymer of spherical shape. The resin is prepared by nuclear sulfonic acid groups attached to a common matrix. The sulfonic acid groups are highly hydrophilic, and bind water tightly inside each resin bead. The moisture content decreases as percent crosslinkage increases. By interpolation of a standardized curve, 50W-X4 has a moisture content of approximately 70 percent.

Resins with 1 to 4 percent divinylbenzene content, as compared with higher crosslinked resins, are characterized as follows:

1. High degree of permeability.
2. Contain a large amount of moisture.
3. Capacities are lower on a wet volume basis.
4. Equilibrium rates are high.
5. Physical stability is reduced.
6. Selectivity for various ions is decreased, but ability to accommodate larger ions is increased.

Resins in the 50 to 100 mesh (or finer) range, compared to coarser resins, have the following characteristics:

1. The time required to reach equilibrium is decreased.
2. The flow rate decreases.
3. The pressure drop across an ion exchange column increases.

4. The bed expansion during a backwash cycle is greater.
5. The efficiency of a given volume of resin increases or the volume of resin required to perform a specific operation is decreased.

APPLICATIONS OF ION EXCLUSION IN THE SUGAR INDUSTRY

For years, the sugar industry has used the process of carbonation as a means of purifying sugar juices. The process has many advantages, but possesses severe limitations as well. Such juice impurities as monovalent mineral salts, the anions of amino acids, and other organic acids are present in large amounts, yet are relatively untouched by carbonation purification.

Over the past several years, decreased sugar recovery and increased molasses production has brought about a need for methods of increased and better impurity elimination. Since maximum sugar recovery must be accomplished, and since carbonation alone cannot presently be eliminated (due to the economy of the process), the need exists for supplementary purification.

The process of ion exclusion (especially since the advent of the Higgins continuous contactor (9)) has been given serious consideration as the possible solution to the aforementioned problem. (1, 2, 3, 4, 5, 9)

If the crosslinkage of the resin is controlled to the right degree, the sugar molecule will enter the bead, but larger molecules, such as color bodies, will be excluded. Sodium and potassium salts, amino acids, etc., are excluded due to the Donnan membrane effect.

The sugar juices should be softened or converted to monovalent form, prior to exclusion. This step must be done first, so that the resin does not become loaded with multivalent ions, such as calcium. If this were to occur, the resin would become useless, and the exclusion apparatus would have to be shut down while the resin was cleared.

The process of ion exclusion has several benefits to offer the sugar processor. As stated earlier, ion exclusion can eliminate ionic impurities not removed by carbonation. Some buffer capacity will be maintained in the juice due to the degree of purification (about 50 percent). Sugar extraction, of course, can be increased. Scaling of evaporator tubes should be virtually eliminated, as calcium is removed in the softening step. Since color bodies are excluded, improved sugar color will be evident. There is a possibility of improved crystallization, since high molecular weight impurities should be removed to a great extend. There is no need to cool the solution and reheat it (a costly process) since the ion exclusion is run at high temperatures. Water alone is required to "regenerate" the ion exclusion resin. The resin itself is a very stable one and should last quite awhile.

ION EXCLUSION EXPERIMENTS

U.S. Patent No. 3,214,293, issued to Mountfort (2), reveals some interesting data concerning the application of the ion exclusion process to affination syrup. Ion exclusion, in conjunction with sugar processing, was covered in the literature to some extent some years ago (3, 4) but there are only a few recent references (1, 2, 5, 9), one of which is the Mountfort patent(2).

The present authors had the opportunity on separate occasions to personally interview G. Mountfort and D. Sutherland on the subject of their work. Based on those interviews, published data, and a visit to Colonial Sugar Refining Company in Sydney, Australia, it was felt that research work into ion exclusion, as used on blackstrap molasses, might prove fruitful. Since Mountfort and Sutherland's work was so well documented and lucidly reported, it was felt that any research pilot plant should be "tuned in" by retracing their work on affination syrup before proceeding to blackstrap experiments.

The Chicago plant of SuCrest Corporation was most helpful in providing sample quantities of both affination syrup and blackstrap molasses for the experiments.

Analysis of these samples was as follows:

	Affination syrup	Blackstrap molasses
Brix	74	80
Ash, percent	0.25	5.5
Pol	74	50
pH	7.0	5.5

The pilot plant setup finally adapted is illustrated in the flow scheme contained in figure 1. Resin columns were 6 inch diameter lucite. Filters, of course, were from Industrial Filter & Pump Mfg. Co. Most other vessels and mixers were stainless. Most interconnecting pipe was PVDC and valves were stainless.

Since the input samples were received at high Brix, they were first "cut" to 60 Bx with tap water (Chicago water — about 8 grains/gallon hardness). The reason for the "cutting" was the temperature limitation that resulted from the use of the lucite

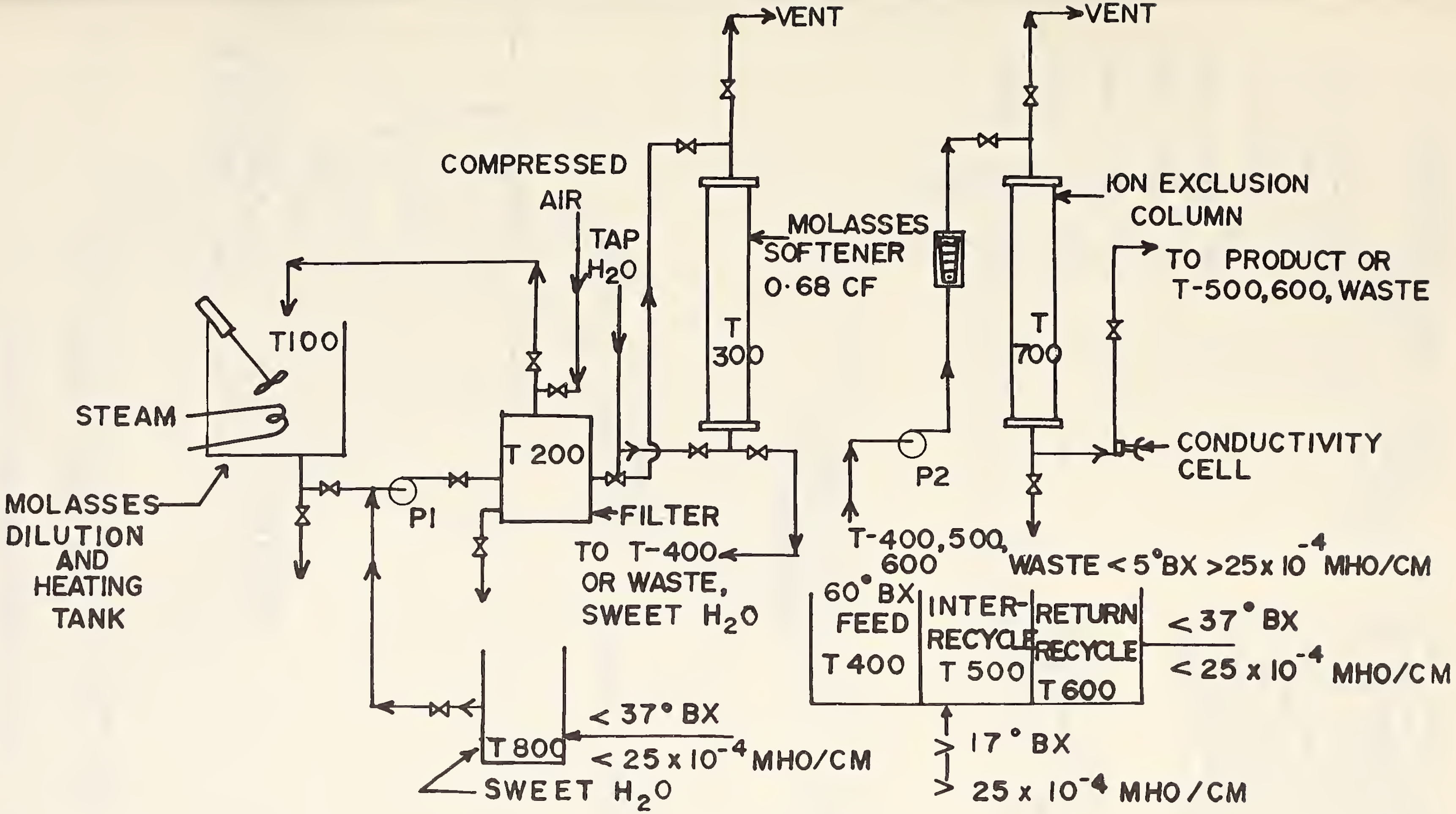

Figure 1. — Schematic of ion exclusion apparatus.

column. During the "Affination Series," it is interesting to note that dilution during the softening step was almost exactly the same percentage as that reported by Mountfort (2). Specifically, 80.4 Bx affination syrup was "cut" to 60 Bx, then fed to a sodium cycle cation exchanger to convert cations to monovalent form. Effluent Bx was 40. This 40 Bx "softened" effluent became the ion exclusion influent. All feeds were first heated to 130°F. The resin used for the softening step was INDUSTRILITE-10. The resin used for the ion exclusion step was Dowex 50W-X4.

The steps in an ion exclusion cycle are shown in table 1, and the results shown in the following figures. Figures 2, 3, 4, and 5 show, first, a theoretical ion exclusion cycle and following that, 3 typical actual

Table 1. — Sequence for Ion Exclusion

Step	Bed Vol.	Oz.	U.S. Gal.	From	To
1	0.16	101.0	0.79	T-400	Waste
2	.15	94.7	.74	T-500	Waste
3	.02	12.6	.099	T-500	T-500
4	.15	94.7	.74	T-600	T-500
5	.11	69.5	.54	T-600	Product
6	.05	31.6	.25	H_2O	Product
7	.26	199.0	1.55	H_2O	T-600

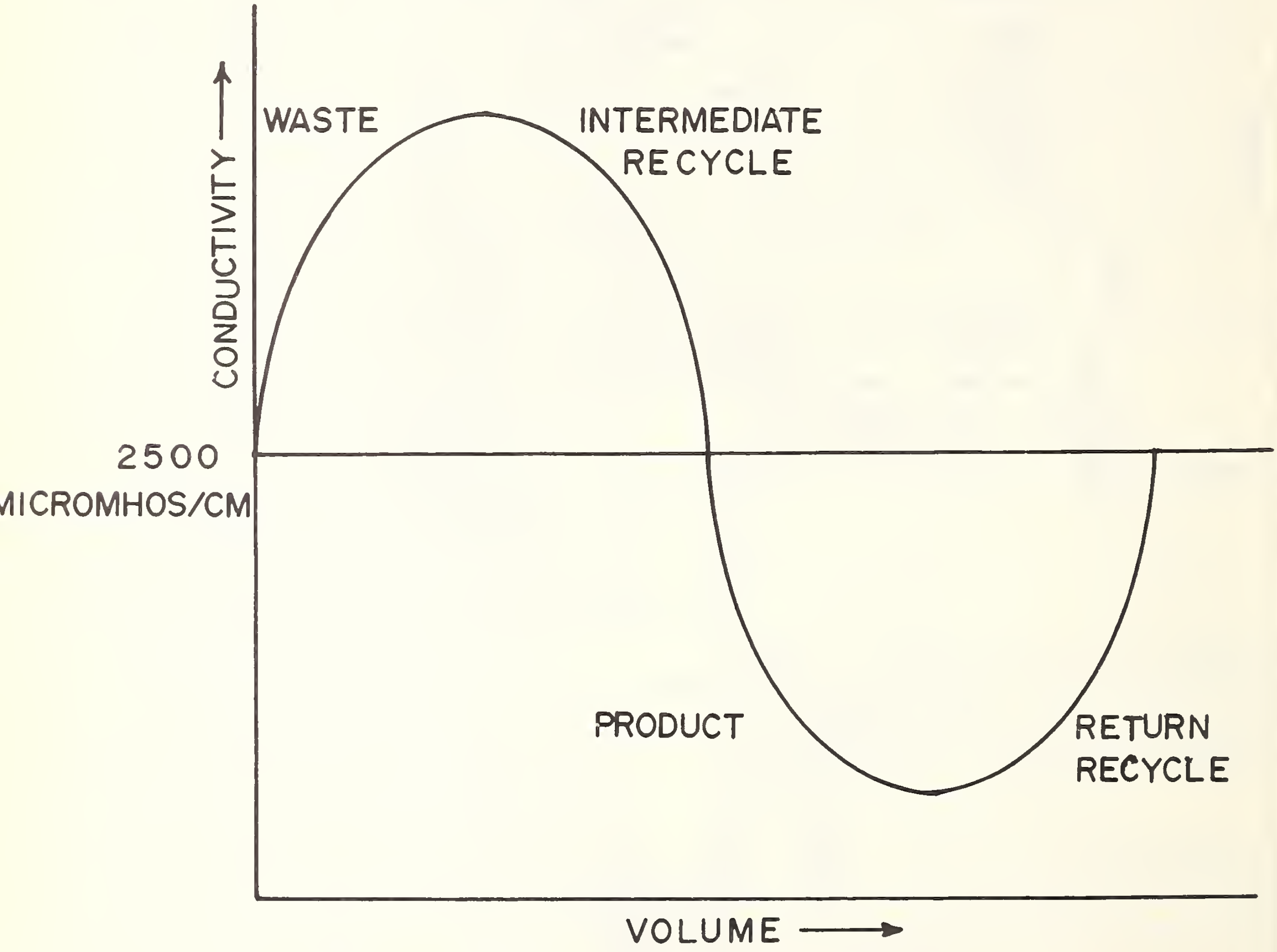

Figure 2. — Theoretical ion exclusion fraction breakoff points.

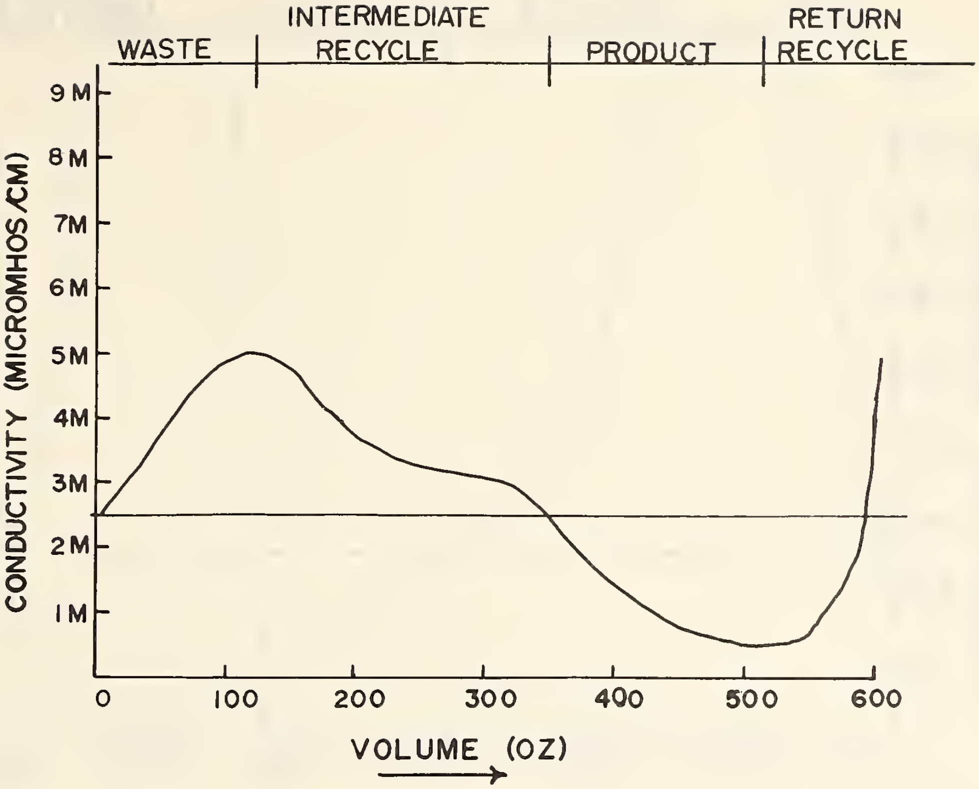

Figure 3. — Actual ion exclusion. Cycle No. 1, affination syrup.

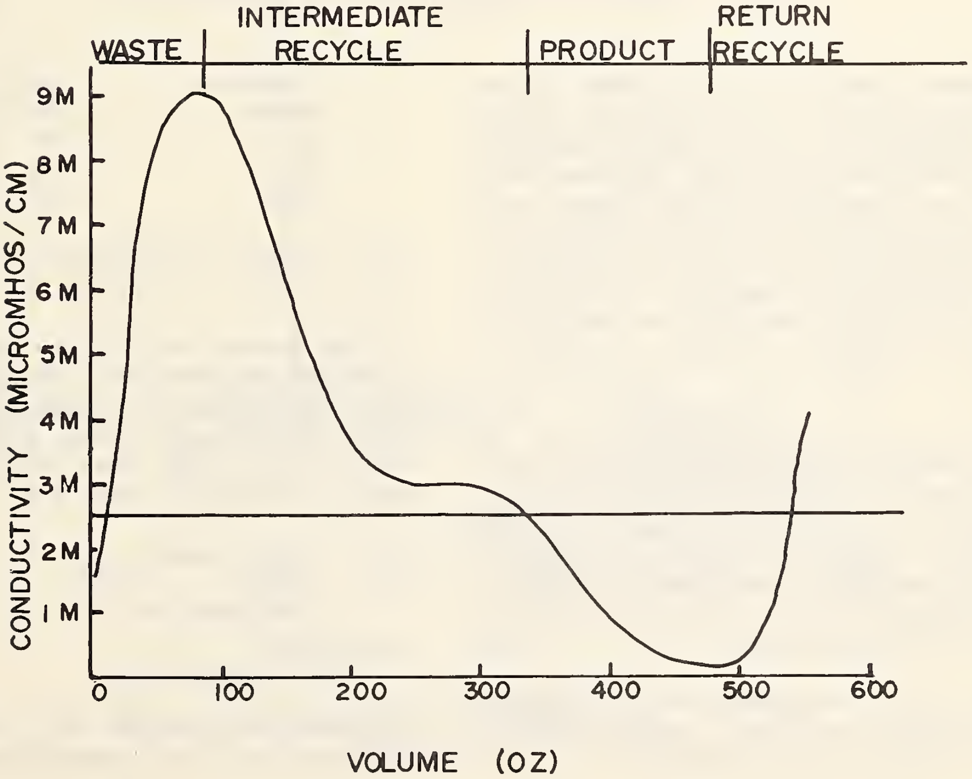

Figure 4. — Actual ion exclusion. Cycle No. 2, affination syrup.

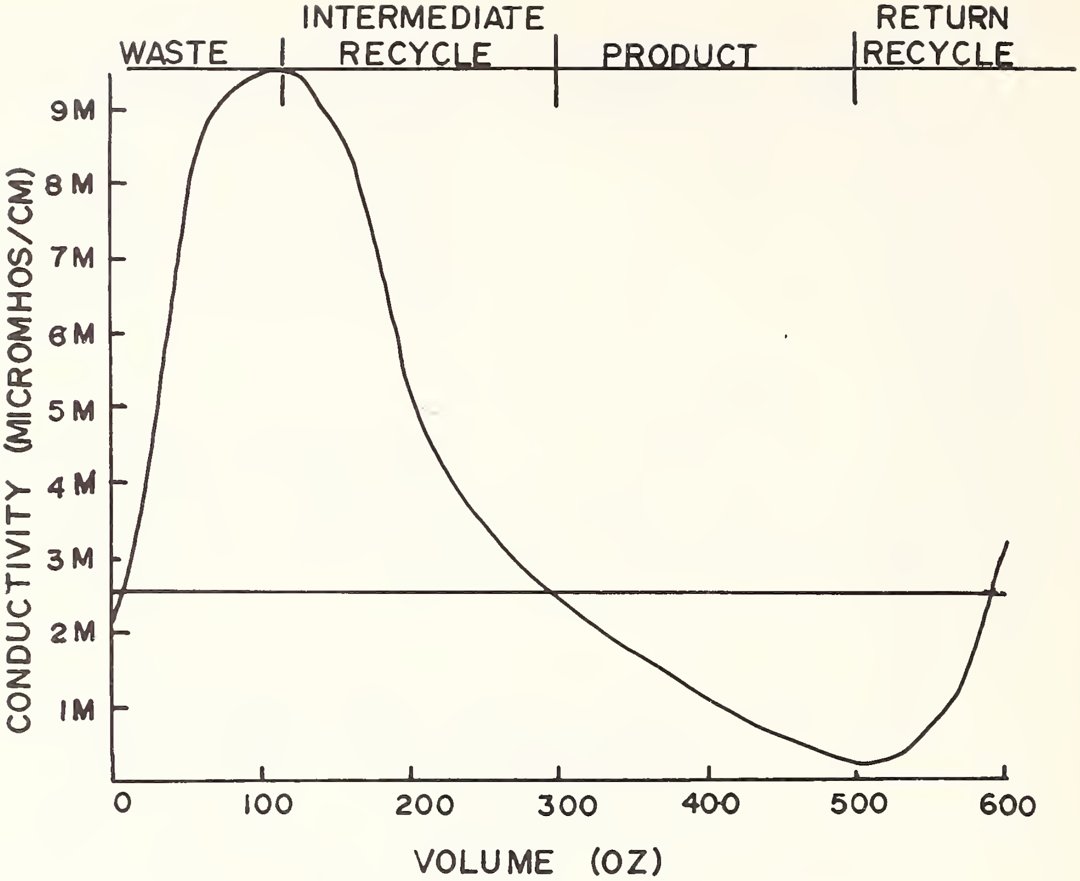

Figure 5. — Actual ion exclusion. Cycle No. 3, affination syrup.

cycles selected from the total included in the experiment. In short, the conductivity readings and the "cut" proportions pretty well confirmed Mountfort's readings. It should be noted that the first process cycle data indicated a greater than expected "product cut," but this was due to the fact that the staff performing the work were basing their "cut" only on conductivity, rather than on both conductivity and density. Correction of this operating procedure brought the developed data into close correlation with that of Mountfort.

It remained then to switch pilot-plant feed to blackstrap molasses. The 80 Bx molasses was cut to 60 Bx and softened. The feed to ion exclusion was 40 Bx. Final product off ion exclusion averaged 26 Bx (35 percent dilution). Figures 6, 7, 8, and 9 are typical conductivity curves for test runs. Figure 10 is a typical density curve. Figure 11 is a conductivity curve and figure 12 is another density curve.

Samples of the ion exclusion treated blackstrap molasses were sent to SuCrest Corporation Chicago laboratories. Their analysis was as follows:

Sulfated ash	0.015 percent
Density	27 Bx
Pol	18
pH	4.8
Color	31° Stammer

In a nutshell, the product looked like a reasonably pure one, but one with relatively high color.

It was reasoned that the same NaCl necessary for regenerating the cation resin "softener" could first be used to regenerate an anion decolorizing resin column. Accordingly, the original research project was extended and a series of anion resin decolorizing tests was initiated. As previously noted, feed to anion resin was:

Approx. 26 Bx
130° F.
0.015 percent ash
pH 4
31° Stammer Color

Resin used was new IRA 401S, with which our company has had good success in the past.

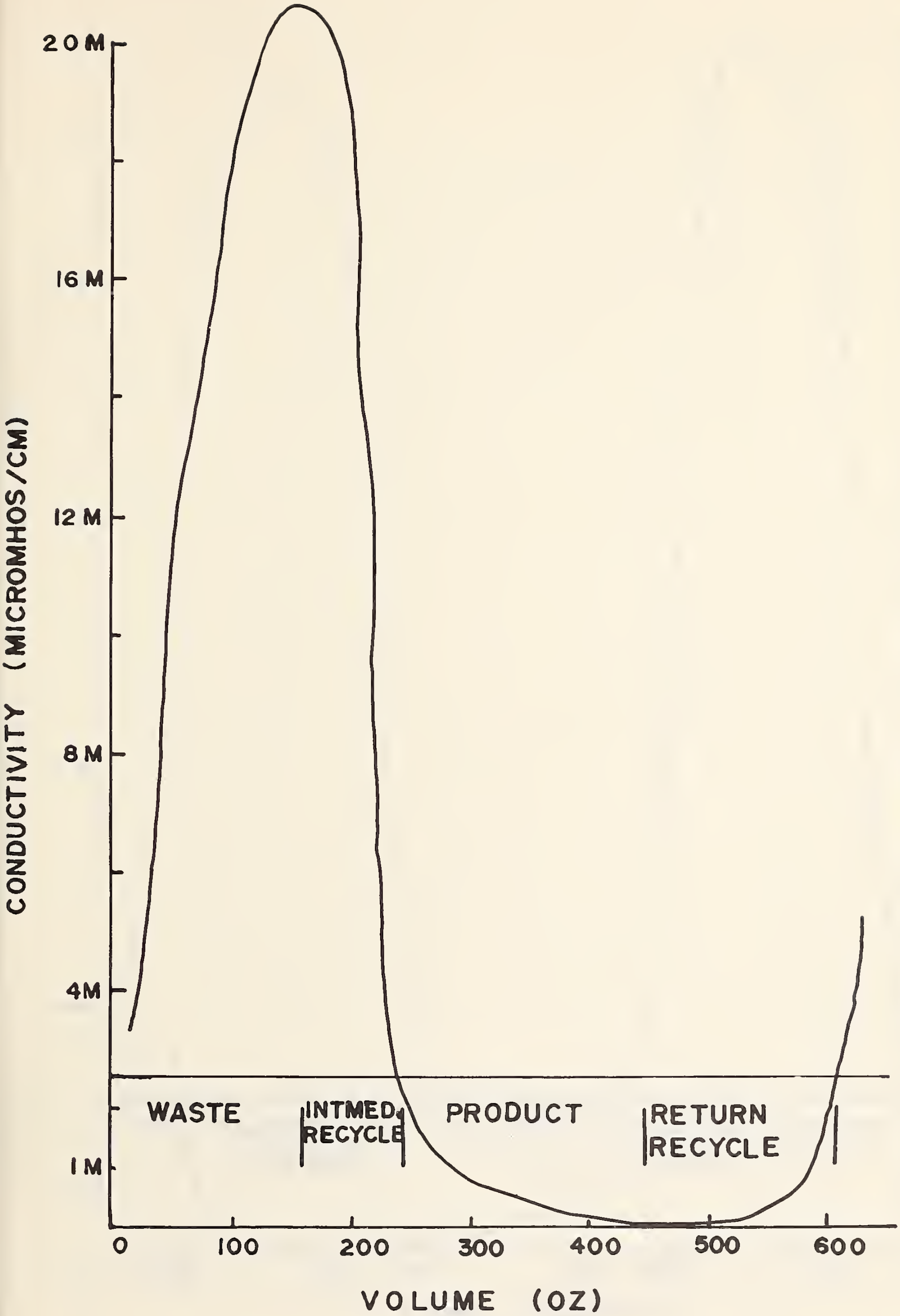

Figure 6. — Conductivity in blackstrap cycle No. 1.

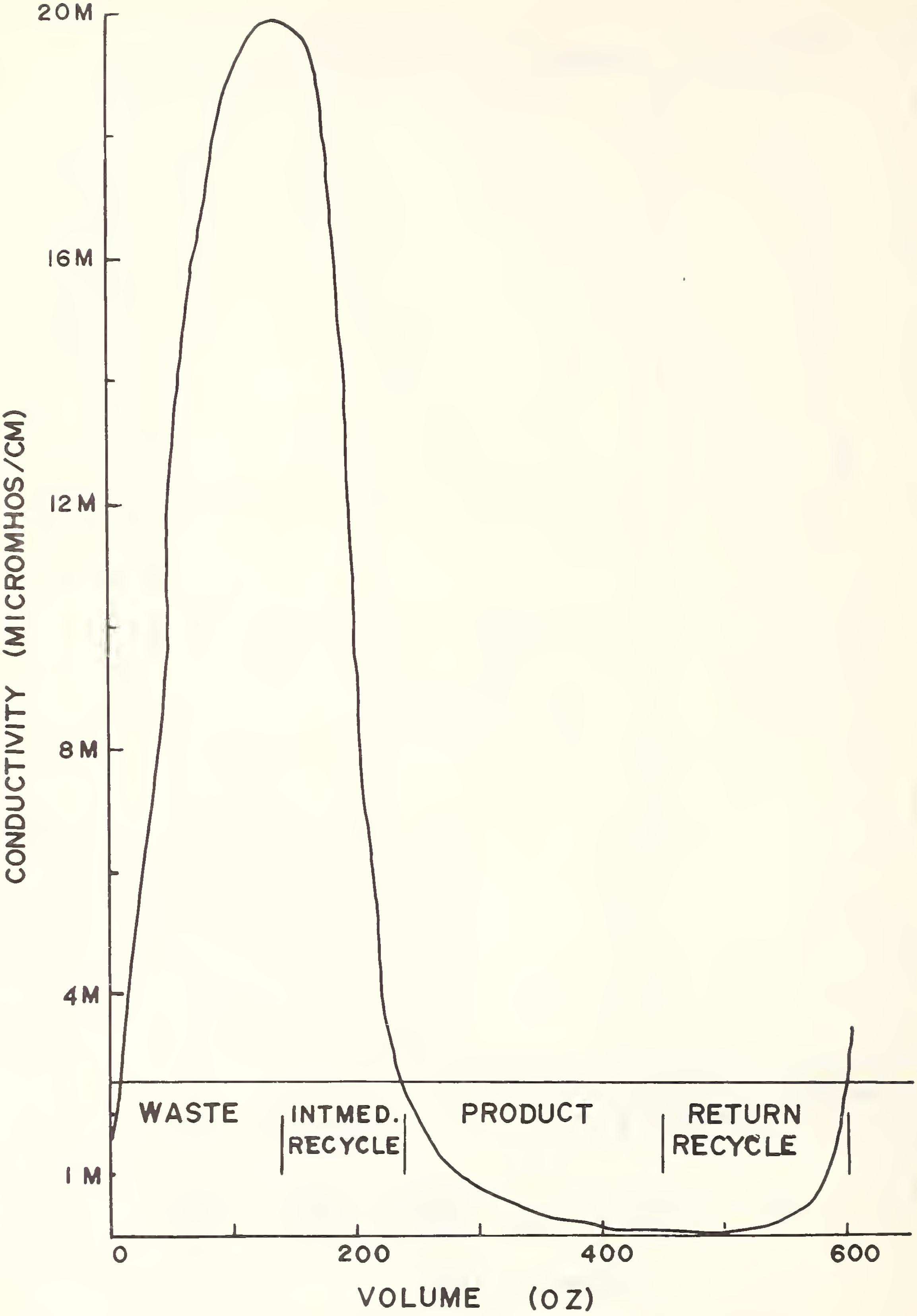

Figure 7. — Conductivity in blackstrap cycle No. 2.

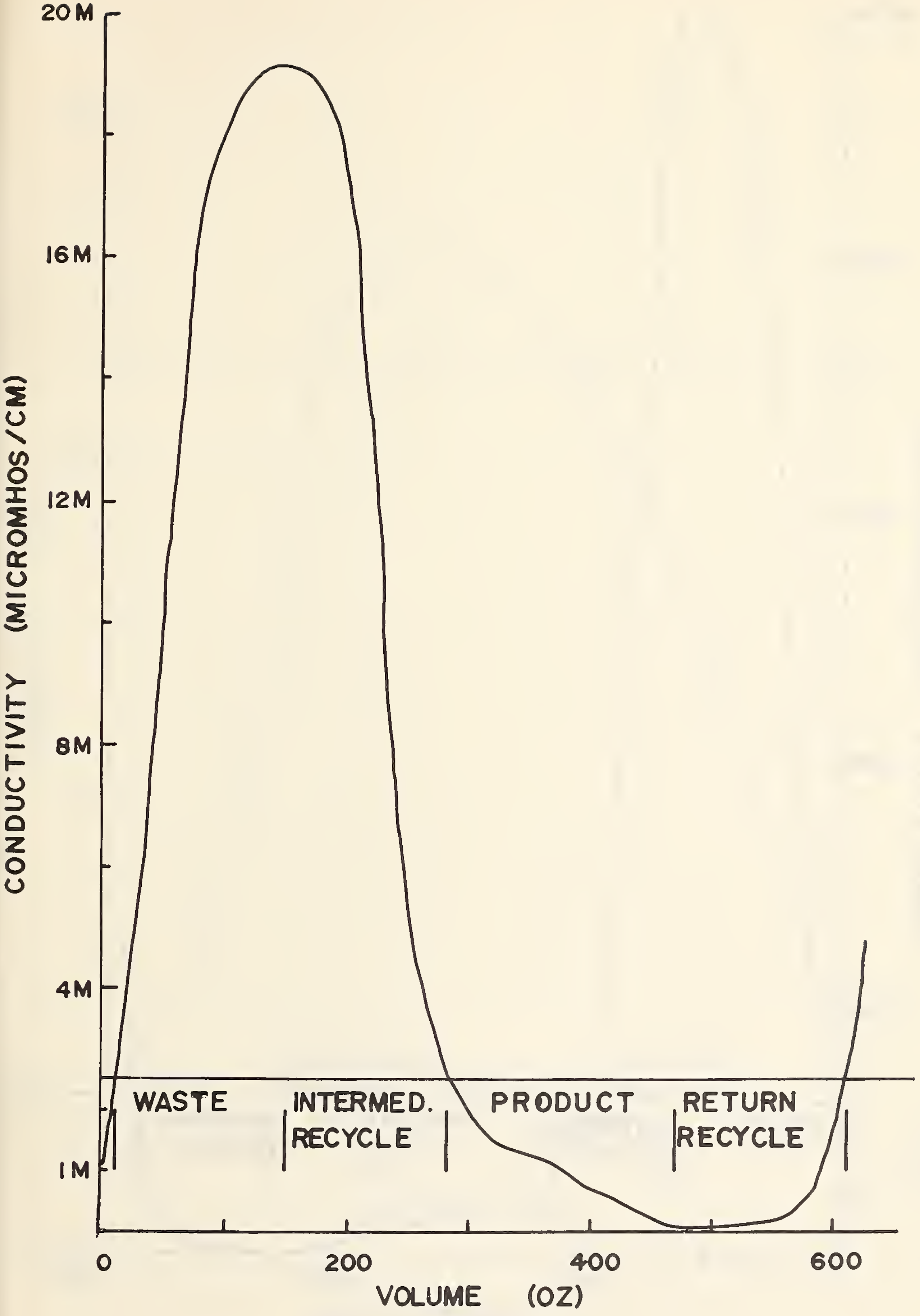

Figure 8. — Conductivity in blackstrap cycle No. 3.

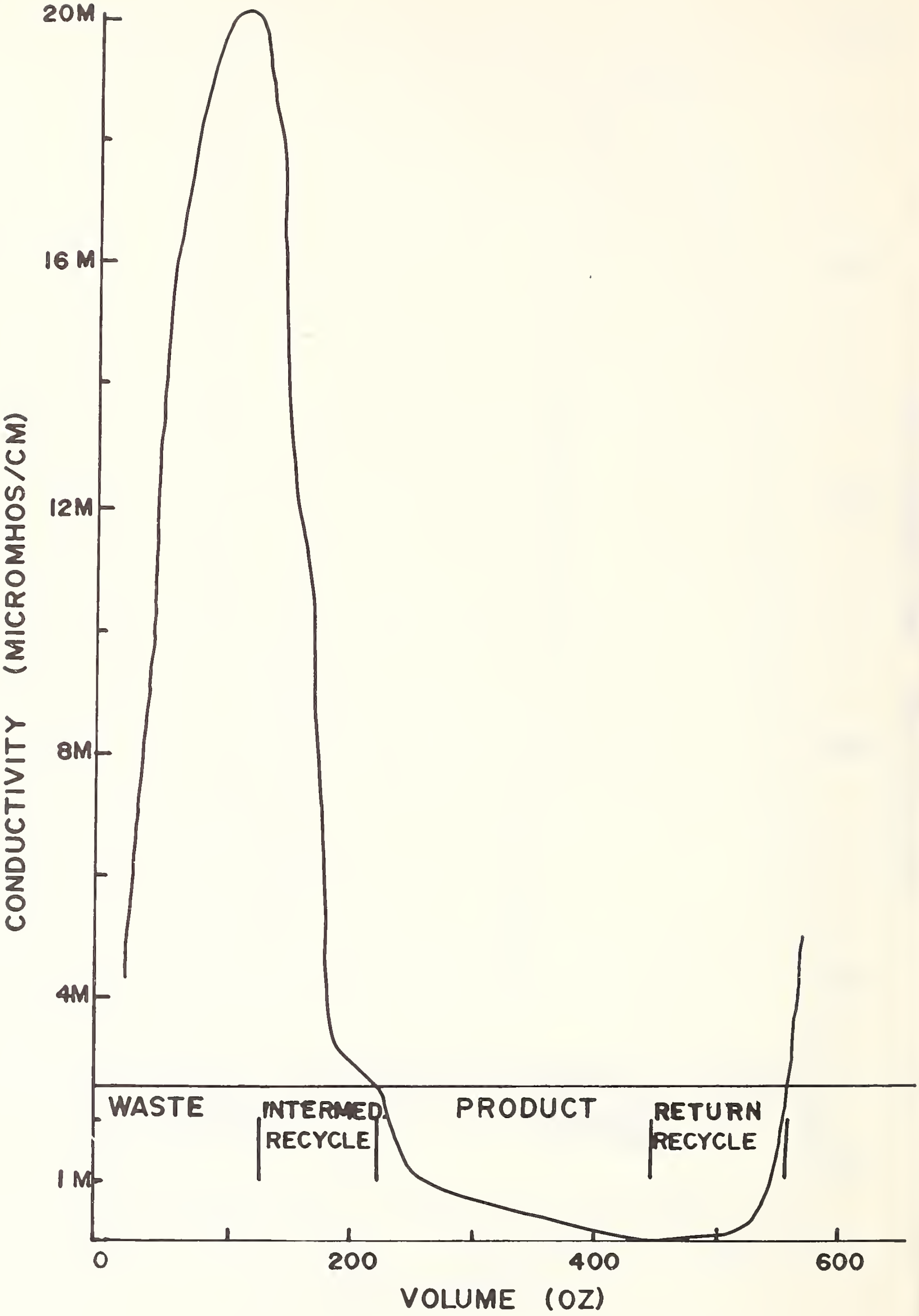

Figure 9. — Conductivity in blackstrap cycle No. 3A.

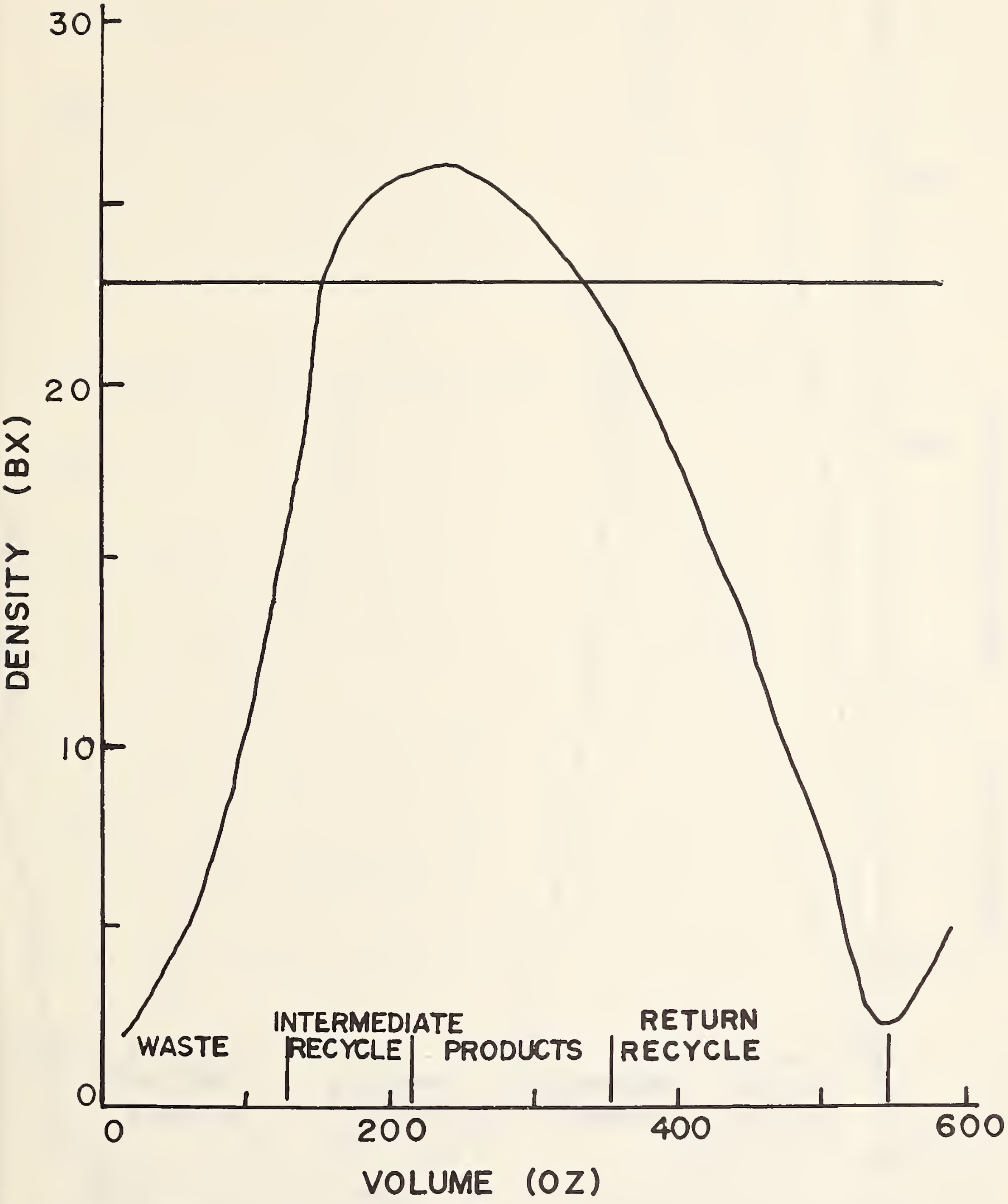

Figure 10. — Density in cycle No. 1A, blackstrap molasses.

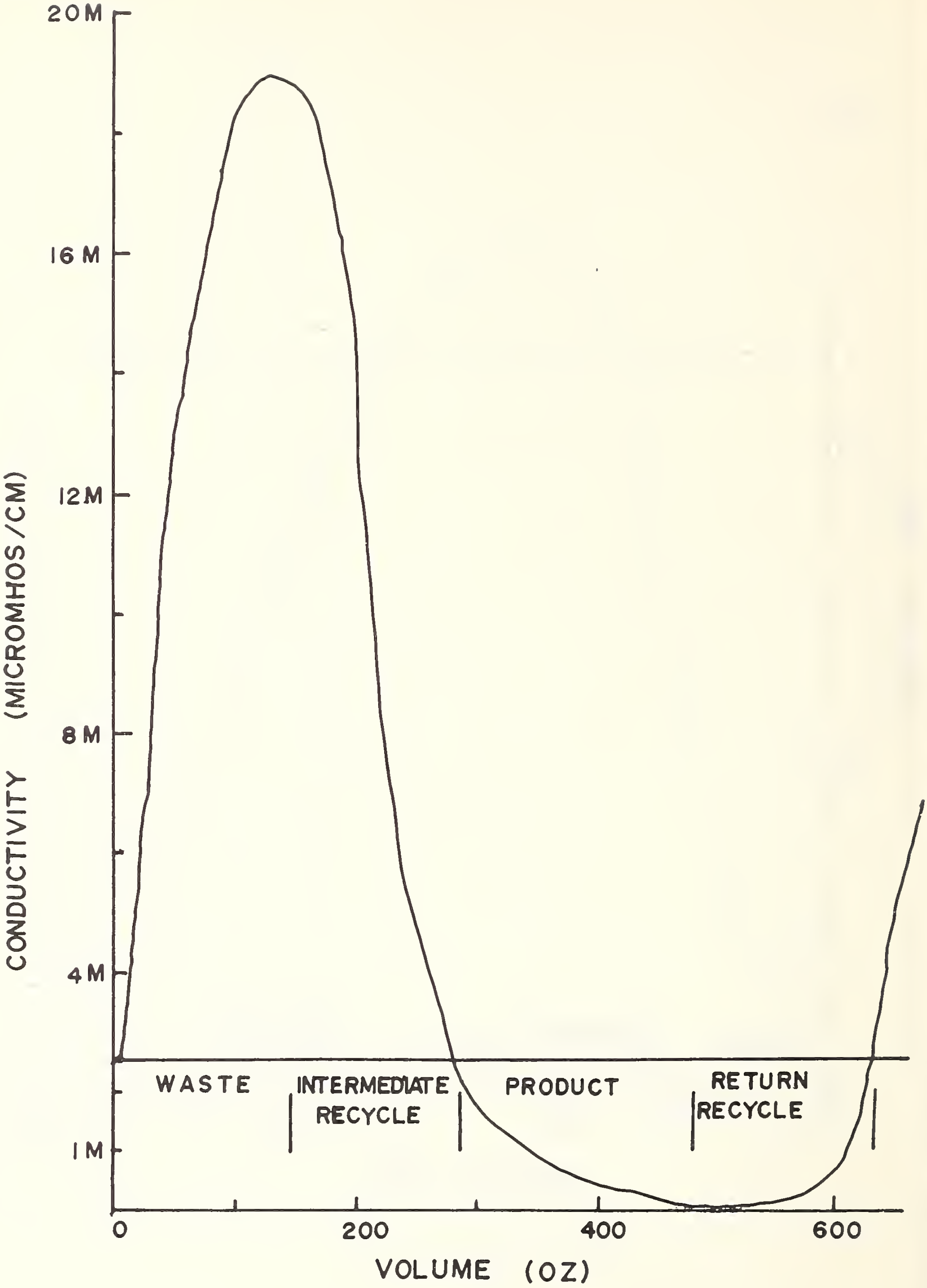

Figure 11. — Conductivity in blackstrap cycle No. 2A.

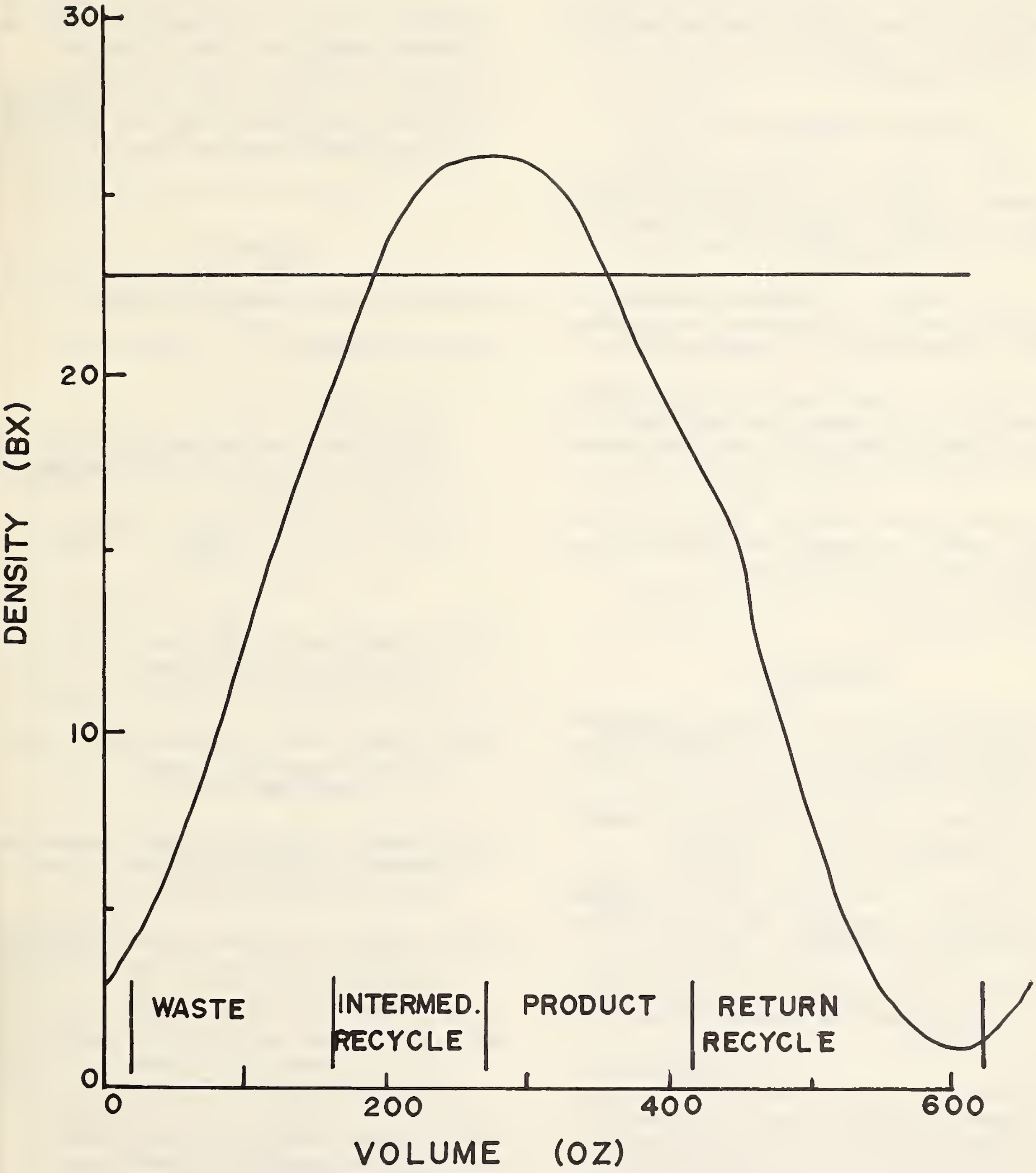

Figure 12. — Density in blackstrap cycle No. 2A.

In brief, operating on the ion excluded affination syrup, approximately 50 bed volumes were processed to an end point of 40 percent color removal. We believe this might be improved, because flow rates (BVH) were somewhat higher than normal factory practice (laboratory error).

Operating on ion excluded blackstrap molasses, approximately 30 bed volumes were processed to an end point of 40 percent color removal. Flow rates were within expected ranges.

COMMENTS AND CONCLUSION

1. Ion exclusion is a process that must be reexamined — especially for very impure feeds; in fact, perhaps the process has suffered because of ill considered early sugar applications.

2. When applied to blackstrap molasses, ion exclusion, followed by decolorization, can produce a potential liquid invert sugar at a very low total cost.

3. Some of the color bodies remaining in the ion excluded product are apparently not easily removed by anion resin and either activated carbon or a specially selective cation resin will have to be considered.

4. Double use of regenerant NaCl (or sea water) greatly reduce overall cost of full utilization of ion exchange resins in the selected instance.

Patents applied for.

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APPENDIX

Ion exclusion sequence calculations (slide rule).

Ion exclusion columns:

I.D. = 5.50 in.
R = 2.75 in.
Pack column to wet resin depth of 48.00 in. = H
Bed Volume (B.V.) = $\pi R^2 H = \pi(2.75\text{ in.})^2 \times 48.00\text{ in.} = 1138\text{ in.}^3$

$$\text{B.V.} = 1138\text{ in.}^3 \times \frac{1\text{ oz.}}{1.80\text{ in.}^3} = 633\text{ oz.}$$

Step 1: Influent: feed; effluent: waste.
0.16 B.V. from T-400; to waste
0.16 × 633 oz./B.V. = 101 oz.

Step 2: Influent: inter-recycle; effluent:waste.
0.15 B.V. from T-500; to waste.
0.15 × 633 oz./B.V. = 94.7 oz.

Step 3: Influent: inter-recycle; effluent: inter-recycle.
0.02 B.V. from T-500; to T-500
0.02 × 633 oz./B.V. = 12.63 oz.

Step 4: Influent: return-recycle; effluent: inter-recycle.
0.15 B.V. from T-600; to T-500
0.15 × 633 oz./B.V. = 94.7 oz.

Step 5: Influent: return-recycle; effluent: product.
0.11 B.V. from T-600; to product
0.11 × 633 oz./B.V. = 69.5 oz.

Step 6: Influent: return-recycle; effluent: product.
0.05 B.V. from T-600; to product
0.05 × 633 oz./B.V. = 31.6 oz.

Step 7: Influent: water; effluent: return-recycle.
0.26 B.V. from water; to T-600
0.26 × 633 oz./B.V. = 199.0 oz.

Calculations for NaCl requirement to change 50W-X4 from H^+ to Na^+ form.

Ion exclusion column.

$$\text{Resin volume} = 1138\ \text{in.}^3 \times \left(\frac{1\ \text{ft.}}{12\ \text{in.}}\right)^3 = 0.659\ \text{ft.}^3$$

NaCl required

25 lb. NaCl/ft.^{3} resin × 0.66 ft.^{3} resin = 16.47 lb. NaCl

H_2O required. (12% NaCl solution).

$$\text{Total Soln. weight} = \frac{16.47\ \text{lb.} \times 100\%}{12\%} = 137.2\ \text{lb.}$$

Water weight = 137.2 - 16.47 = 120.73 lb.

Water volume = 120.73 × 1 gal./8.30 lb. = 14.50 gal.

Flow rate required, (to regenerate in 1 hr.)

$$14.50\ \text{gal./hr.} \times \frac{1\ \text{hr.}}{60\ \text{min.}} = 0.242\ \text{g.p.m.}$$

Contingency factor:

Bring water volume to 20 gal.

20 - 14.5 = 5.50 gal. additional water.

$$\text{Additional salt: } \frac{16.47\ \text{lb. NaCl}}{14.50\ \text{gal. } H_2O} \times 5.50\ \text{gal. } H_2O = 6.25\ \text{lb. NaCl}$$

Total Solution:

16.47 + 6.25 = 22.72 lb. NaCl/20 gal. H_2O

Resin volume correction.

Resin height went from 48.00 in. to 35.25 in. after 1 hr. wash with 12 percent NaCl solution. This was a drop of 12.75 in. To bring the resin level back to 48.00 in., the following amount of resin must be added:

$$12.75\ \text{in.} + \frac{12.75\ \text{in.}}{48.00\ \text{in.}} \times 12.75\ \text{in} = 16.14\ \text{in.}$$

NaCl solution requirements for additional resin.

Additional resin volume = $\pi R^2 H$ =

= π (2.75 in. × 1 ft./12 in.)^2 × 16.14 in. × 1 ft./12 in. = 0.212 ft.^{3}

Additional salt:

$$0.212\ \text{ft.}^3 \times \frac{25\ \text{lb. NaCl}}{1\ \text{ft.}^3} = 5.55\ \text{lb. NaCl}$$

Additional solution weight

$$5.55\ \text{lb. NaCl} \times \frac{100\%}{12\%} = 46.2\ \text{lb.}$$

Additional water

46.2 lb. solution — 5.55 lb. NaCl = 40.65 lb. water

40.65 lb. water/ 8.30 lb./gal. = 3.45 gal. water

Flow (to regenerate in 1 hr.):

3.45 gal./hr./60 min./hr. = 0.0575 g.p.m.

This flow rate is impractical, so double the above quantities were used.

DISCUSSION

G. W. MULLER, JR: I'm interested in the end product — the flavor and taste. Do you have any idea how it compares to a typical molasses? Is it edible? Is it useful for soft sugars? What would it be like?

J. F. ZIEVERS: It looks and tastes like liquid invert.

C. J. NOVOTNY: To the extent that we carried it last week, there's still some color left, as we said. If your products have to be water white, then you're going to have to do something more to it.

F. G. CARPENTER: Why won't ion exclusion work on high purity liquors?

C. J. NOVOTNY: You're dependent on a sort of bulk separation of the sugar molecule from the non-sugar molecule and you will get most of the sugar inside the pores of the resin bead with perhaps half or a third of the non-sugars present. It depends on the relative size of the molecules. The main reason that ion exclusion works on sugars is that the sucrose molecule will fit into the resin pores and the non-sugars are excluded from fitting into the resin pores, and a high-purity sugar is likely to have not so many large molecules around, other than ash. Ash will go into the bead pretty well.

W. R. TUSON: With such a dirty feed, what sort of fouling experience would you have with your softening bed? Maybe you didn't run enough cycles to be able to answer this, but in your conversations with Mountfort and Sutherland, did you have any indication about this sort of behavior?

C. J. NOVOTNY: You're right, we ourselves did not run enough cycles to determine that in our lab; however, cation resins are very difficult to irreversibly foul. The Mountfort and Sutherland work is reported in the literature.[1]

W. R. TUSON: I was not thinking of that type of fouling as much as of bed fouling, because of the nature of the feedstock that you have. In other words, did you have severe dropoffs in flow rate on your softening column which made it require rather short cycles?

C. J. NOVOTNY: No, we didn't notice that. However, we did use good tight filtration ahead of it.

W. R. TUSON: You would have to prefilter, in order to protect your softening bed?

C. J. NOVOTNY: I think you probably would. We've given some thought to running so-called "dirty feed" on upflow continuous ion exchange equipment, in the sugar field and in other industries. I don't think we can say, as yet, that you can get by without it. I think you have to test any particular feeds. In this instance, I think you should plan on filtering.

W. R. TUSON: Can you make any comment with respect to the estimated useful life of your ion exclusion resin. You mentioned physical stability as being a factor with the crosslinked cation resins that you use.

C. J. NOVOTNY: No, I don't think that I can. However, again the cation resins are the most physically stable of the two or three kinds of resins around. The osmotic shock is pretty great — it varies from as much as 40° Bx to 0° Bx, on a regular alternating cycle.

S. B. SMITH: When you come in with sugar following water, do you bring the sugar in the bottom of the column or is it operated downflow?

C. J. NOVOTNY: It's all downflow. You can illustrate ion exclusion for yourself very easily by simply taking a 60° Bx sugar solution, putting it into a beaker full of resins and then pouring it back out. It will probably measure 25° Bx. The sugar molecule itself just goes into the pores of the resin.

S. B. SMITH: Do you get any density effect wherein the sugar goes down one side of the column too fast?

C. J. NOVOTNY: Well, I think that that's a matter of distribution — of hardware design. Of course, our columns were pretty small, and it's really easy to distribute well in a column of that size, but that's an important consideration — the hardware.

R. E. ANDERSON: I was fortunate enough to be a member of the laboratory that did the original work on ion exclusion (8)[2]. There seems to be a fair amount of confusion about what the actual process is. I don't think it would be an imposition to give you a short discussion of what ion exclusion is, how it works, and where it applies.

There are three kinds of volume in an ion exchange resin. There is the interstitial volume, which is the volume of water outside the beads. This amounts to approximately 40 percent of the total volume in the column. The beads themselves are made up of two volumes: one of solids, and one of water. Most beads are about 50 percent water, so an average set of values is:

Outside volume:	40 percent
Solids volume:	30 percent
Inside volume:	30 percent

Now, if you put a solution on top of this bed and run it down through it, the time at which a given solute comes out at the bottom will vary directly with the volume its solution has to displace to get to the bottom. There are various types of solutes. We can have highly ionized solutes such as sodium chloride. In this case, we have a phenomenon familiar to all who have taken beginning physical chemistry: the Donnan membrane exclusion. This says that if you have a membrane with fixed ionic charges on one side and you put a salt solution outside this membrane, then at equilibrium, the salt solution will have a higher concentration outside than inside the system. You can consider an ion exchange resin bead as a spherical membrane with fixed ionic charges inside. If you put an ion exchange resin in a salt solution, the salt concentration outside the bead at equilibrium will be higher than inside — at most concentrations, by about 10 to 1. That is, the salt would be 10 times more concentrated outside than inside. This is shown in figure A, line (1). If we think of something non-ionic, like methanol, acetone, or a similar water-soluble component, it will not be affected by the Donnan membrane effect. Its concentration should be essentially equal inside and out. This is line 2 in figure A. In the sugar system, sugar is not ionized, and so, if we can make the resins open enough for the sugar to get in and out, sugar will follow line 2, while the ash or inorganic salts will follow line 1. We are fortunate in that the colorants are generally larger than the sugar and are also ionized to a certain extent, so they will tend to follow 1. A component that follows line 2, i.e., a non-ionic component, essentially has to displace 60 percent of the bed volume, while an ionic component that follows line 1 only has to displace the interstitial volume of 40 percent to get to the bottom. Let us put a mixture on the top of the column and look at the concentration versus volume coming out the bottom. The bed is full of water, so no solute will come out for awhile. Then, if you have square wave phenomena as in line 1, figure B, the ionic material will come out, and some time later, the non-ionic material. If the increment of feed is small enough, you can have the ionic material all out before the non-ionic gets to the bottom. We have just put a slug of mixture on the top and washed it through with water. In practice, we do not get square wave, we get line 2, figure B. So you are diluting the product, and getting separation at the expense of dilution.

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[1] Sutherland, D.N., and Mountfort, C. B. 1969. Indus. Engin. Chem., Proc. Design Development 8:75.

[2] Asher, D. R. 1956. Indus. Engin. Chem., 48: 1465.

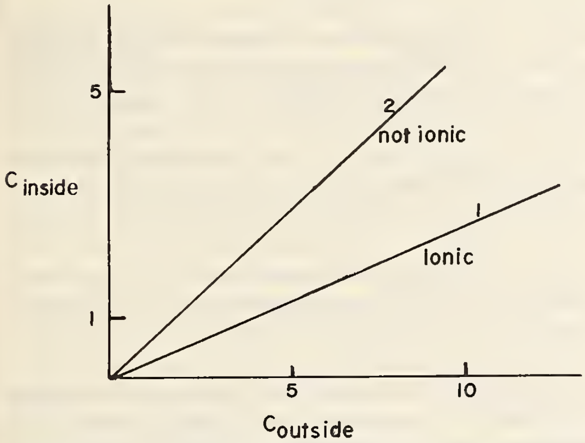

Figure A. — Concentrations inside and outside ion exchange beads

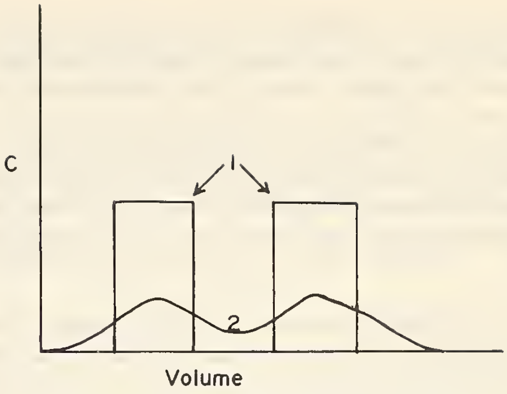

Figure B. — Ion exclusion effluent

Ion exclusion, as originally conceived, in early experiments did not seem to work on sugar because 8 percent crosslinked resins were used. Later, it was found that when a lower crosslink was used, sugar could be separated from the salts. However, the problem in going to lower crosslinked resins is that if you go too low, the salt-exclusion effect becomes less pronounced. Also, the lower the crosslinking of the resin, the more it will shrink as you put your feed on the column, and swell as you wash it out. This effect increases with decreasing crosslinking.

The people who developed the process became very frustrated trying to sell it. It is really a beautiful process, in the right place. I think it deserves a good look.

J. F. DOWLING: In using lower crosslinked resins, do you not produce an excess amount of dust, with a lower osmotic shock?

R. E. ANDERSON: No. They use a fine 50 to 100 mesh resin. The larger the resin, the more susceptible it is to breakage from osmotic shock. When you get to a 50 to 100 mesh resin, it is relatively stable. This is a chromatographic process, and when you think about running chromatographic processes on a large scale, you get scared. The Dow Chemical Company is running ion exclusion on a column 12 feet in diameter. So, it can be done.

J. F. ZIEVERS: As is necessary, of course, when we did the laboratory work, we had to use fixed columns and small columns. Now, looking toward practical applications of what we are showing here, and taking into account some of the questions that came earlier from the floor here, I think Chuck agrees with me that this type of process, theoretically at least, is best fitted to a continuous contactor, or a pulsing contactor of some type, where throughout the loop or the contacting system, at any given point, you are in a state of equilibrium. Therefore, some of these expansions and contractions will not be as pronounced, because they will be at various points in the loops. A lot of the problems, with dirty feed, for example, then can be taken care of by equipment design.

J. F. DOWLING: Can you give me figures on the non-sugars in the molasses on and off? How much are you removing?

C. J. NOVOTNY: I do not have those figures here.

J. F. DOWLING: I think that would be a good figure to know, before going on to the next step.

C. J. NOVOTNY: That is a good point. If you have an idea what a typical molasses is, in non-sugars, then that is very basically the input that was fed to this system after filtration and dilution.

J. A. METZLER: You apparently did not keep material balances of the components, did you?

C. J. NOVOTNY: That's right, we did not.

J. A. METZLER: I noticed you had 1.17° Bx going to the sewer, and I was wondering if you had any idea how much of that was sugar. The second point I was trying to find out was how much evaporation is involved in this sort of process. You did not keep the material balance then.

C. J. NOVOTNY: Not in the work we did so far. We still do intend to do quite a bit more. Perhaps at the next meeting we can show you what we have done in the interim.

P. F. MEADS: You made reference to some ill-conceived earlier applications. I wonder if you have some guidelines in mind to help us at this point.

C. J. NOVOTNY: Well, really the only one to which I made reference was the very first attempt at treating sugar on a large scale, in a beet sugar factory with a brand new kind of continuous equipment that had not been used on anything other than water-softening before. There were a lot of valve mechanical troubles and the like. I think equipment failure in that instance was one of the big problems and caused tremendous dilution of the product. I think ion exclusion, because of it, got a bad name, which it has had difficulty living down since.

P. F. MEADS: I think I have in mind that same application, and I was wondering why that failed. Maybe you can give me the answer.

C. J. NOVOTNY: It is Jim's opinion and mine that the principal reason for its failure was excessive dilution and the resultant expensive evaporation of that dilution water. We also think that the principal cause of that dilution was not so much the fault of ion exclusion, but of the brand new installation, which was practically experimental at that time.

C. T. DICKERT: Would you consider automation as essential to this operation?

C. J. NOVOTNY: Yes, I would. This little setup had two summer students going crazy trying to keep up with it. Automation would be quite a benefit.

C. T. DICKERT: If you use a fixed bed, would this be of normal dimension and similar geometry to conventional ion exchange systems?

C. J. NOVOTNY: It would not be a great deal different from an ion exchange column, except that it would require very little free board.

A. VanHOOK: I have often wondered if we might not find a membrane that would invert this preferential effect, so that if we passed a pure sugar solution through this differential membrane, we might be able to hold back the water, and by that means concentrate the sugar solution. Do you, or does anyone here, have any suggestions in that way?

C. J. NOVOTNY: No, I don't have in that particular instance. There is another process, however, called ion retardation rather than ion exclusion, and it basically works just opposite to ion exclusion. It takes the ionized substances into the bead and keeps the sugar out.

A. VanHOOK: I know that the protein people have a material that holds back water, and in that way they concentrate their solutions. Of course, what I have in mind, as you all know, is the possibility of making supersaturated solutions in that way and thus circumventing the inevitable degradation that you always get when you heat up very concentrated sugar solutions, even for short periods.

P. F. MEADS: You are referring to reverse osmosis.

A. VanHOOK: Yes. Would that be effective for increasing the concentration up into the supersaturated range?

P. F. MEADS: It would take excessively high pressures.

C. J. NOVOTNY: If you are interested, the Holly Sugar Corporation has been working on de-ashing using reverse osmosis, and their main problem seems to be fouling of the membranes. They have had a quite a bit of cooperation from several membrane and equipment companies. The process itself is really ultrafiltration, and so you have to filter to quite a high degree before you can possibly use the membrane. S. E. Bichsel presented a paper on reverse osmosis[3] at the Amer. Soc. Sugar Beet Technol. this past February in Denver.

F. BRUDER: Some years ago, I had the fortunate opportunity to see work on ion exclusion in operation. They used 5 foot depth columns, about 24 inches in diameter and they were working both with affination and blackstrap. Joe Dowling asked how much sugar was entrapped in the waste product. At that time, we had about 25 percent that could not be brought back because of the high ash content and non-sugars that had to be discarded. That was just a column operation. Prior to this, there was another operation, similar to yours, but not a filtration. Its aim was to get the material clear enough to run through a bed of 100-mesh material. It was surprising how well syrups flowed through this 100-mesh. Forty Brix blackstrap went through it rather rapidly, and it did do an effective separation, but the losses were prohibitive, particularly for affination.

W. R. TUSON: On this point, I read the Mountfort-Sutherland patent some time ago, and it seems to me that the key to a successful recovery, to a minimal loss of sucrose, evolved around getting rid of the calcium and magnesium cations and replacing them with sodium. Am I correct in this impression?

C. J. NOVOTNY: If you do not first soften the juice to get rid of the multivalent ions, they will be removed by the ion exclusion column, which is actually a sodium cycle ion exchange resin. These ions take up so much more room and they interfere with the flow of sugar molecules into the pores of the bead.

W. R. TUSON: In fact, this would tend to give you a portion of the sucrose which is not recoverable. This is, I think, the point.

C. J. NOVOTNY: Yes, and it would also negate to a good extent the advantages you would get from ion exclusion. Even with use of a softening column first, it will probably be necessary to run some salt brine through the ion exclusion column periodically.

H. WALLENSTEIN: The waste stream would also present a pretty difficult problem in our days of sensitivity on pollution. You possibly might use it as a source of dilution for your blackstrap, or for your crystallizer syrups, depending on how much of each you have. It is low density, and high in B.O.D. You certainly could not sewer it.

C. J. NOVOTNY: Almost any purification process is going to present some sort of a waste treatment problem because you have to do something with the impurities that you took out. Ion exchange per se, with which we are all more familiar, does the same thing. In that case, not only do you have all your non-sugars being discharged with the waste, but you have extra acid and caustic or ammonia along with them.

Every question ever asked in the history of any of these meetings is an economic question. And it is how much does it cost you to recover sugar this way. If you are going into the overall cost, you are going to have to figure every cost involved, including what it takes to treat the waste. Maybe you can sell the waste. That has been done.

C. T. DICKERT: On the flow rate through the column, I would imagine that you would have to be very careful to avoid much overlap of the ash curve and the sugar curve. Is that a fairly critical factor?

C. J. NOVOTNY: Yes, it is. It is a combination of that and distribution. If you can bring in the various fractions in relatively plug flow, then the flow rate is less critical. Distribution is extremely important.

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[3] Zanto, L. T., Christoffer, L. M., Bichsel, S. E. 1970. A study of some physical and chemical parameters affecting non-sugar — sugar partition with cellulose acetate membrane. Jour. Amer. Soc. Sugar Beet Technol. 16: 26-33.

FOURTH SESSION: Frank G. Carpenter, Cane Sugar Refining Research Project, New Orleans, La., Chairman

IDENTIFICATION OF SUGAR COLORANTS

by

Leon Farber and Frank G. Carpenter
Cane Sugar Refining Research Project
New Orleans, La.

(Presented by Leon Farber)

ABSTRACT

For the first time, a number of cane colorants have been identified. They are all cane pigments that escape the refining processes and some even persist into the refined sugar. These are: chlorogenic acid, caffeic acid, p-hydroxycinnamic acid, 4-hydroxy-3-methoxycinnamic acid, 4-hydroxy-3,5-dimethoxycinnamic acid, kaempferol, and umbelliferone.

Several additional constituents that are not colored have been identified. These are: p-hydroxybenzoic acid, 4-hydroxy-3,5-dimethoxybenzoic acid, and 4-hydroxy-3-methoxybenzoic acid. Fumaric acid and aconitic acid, which were already known to be present in cane sugar, have been located on the high voltage paper electrophoresis separation of sugar constituents.

INTRODUCTION

The identity of the colorant looms as the largest unknown in sugar technology today. For centuries, sugar has been clarified, purified, and refined, always to take out color, yet no one knows what the color is that is being removed. Through the years many ingenious chemists have applied various schemes in an effort to separate, isolate, purify, and identify the sugar colorants. Many constituents such as reducing sugars, amino acids, carboxylic acids, etc., have been identified (8, 16, 17), but no individual colorants have ever been identified.

The colorants in sugar are recognized as coming from three sources. The caramel type colorant comes from the thermal destruction of sucrose. The melanoidin type colorant comes from reactions between amino acids and invert. The third class is pigments from the original plant.

A previous report (6) pointed out that high voltage paper electrophoresis as developed by Gross (9, 10) produced the best separation of plant pigments. This report (6) showed further that the color of the plant pigments was very light yellow, but they could be easily observed on the paper by means of their fluorescence under ultraviolet illumination. An empirical numbering system was devised, and the cane pigments were catalogued and described in terms of their color, fluorescent color, and mobility on high voltage paper electrophoresis. This made it possible to identify them unequivocally, although only by spot number. A brief survey of sugars at various stages of processing showed that only a few cane pigments persisted through all the refining processes and appeared in refined sugar. Those materials that appeared in the refined sugar were, by definition, the most difficult of this class to remove and were emphasized in the present identification studies.

In the present studies several additional separation methods have been employed. This was necessary because paper electrophoresis can accommodate only small (chromatographic) amounts of material. Other schemes such as solvent extraction and thin layer chromatography were used to separate significant quantities of the colorants, and then high voltage paper electrophoresis, to monitor the separations.

The standard conditions for electrophoresis were the same as those used previously (6), namely:

Temperature	15 ±1°C
Paper	Whatman 3 MM
Buffer	0.05 molar sodium tetraborate
pH	9.2
Voltage gradient	100 V./cm.
Time	45 min.

Picric acid (PIC) was used as the mobility standard, and hydroxymethylfurfural (HMF) as the zero marker. Mobilities relative to these standards have been expressed as $M_{HMF\text{-}PIC}$.

In examining the Fluorescence obtained from Ultraviolet excitation of the high voltage Paper ElectrophoroGrams (FUPEG) of many sugars, one spot often stood out. This was spot number 15 in the numbering system at $M_{HMF\text{-}PIC} = 1.00$. Because it stood out so strongly, it received the most attention, and this material was the first sugar colorant identified.

SOURCE OF COLORANT AT SPOT NUMBER 15

Although spot number 15 was always present in refined and raw sugars, upon isolating the actual fluorescencing spot, only a very small amount of material was obtained. Aqueous extracts of cane rind, cane leaves, and bagasse also always contained the material, but again never in any great quantity.

A chance observation that spot number 15 was present in FUPEGs of both coffee and tea led to the fact that an ethyl acetate extract of coffee had a large amount of material at spot number 15, as judged by the brightness of the fluorescence. The material was partially purified by thin layer chromatography on silica gel G. The developing solvent was methanol: benzene: acetic acid (2:11:1). The material at spot number 15 remained at the origin while many other components of the coffee moved away. The silica gel at the origin was scraped off the plate and the colorant was eluted with methanol. The methanol was evaporated under reduced pressure, and the residue was taken up in water and lyophilized, thus effectively removing the last traces of extraneous volatile materials. The material so obtained from coffee in relatively large amounts corresponded exactly with spot number 15 in electrophoresis, and was only slightly contaminated with other coffee constituents.

Thin layer chromatography was used to check further that the material derived from coffee was the same as that derived from sugar. Using the same solvent system as mentioned above, it was found that the component at spot number 15, derived from an ethyl acetate extract of cane leaf (6), also remained at the origin. With the solvent system methanol: acetic acid (1:2), both materials traveled the same distance relative to the solvent front (R_f = 0.73).

During the course of the study of spot number 15 from coffee, it became increasingly apparent that coffee must contain a relatively large quantity of this material. With this in mind, consideration was given to compounds already known to be present in coffee. The most obvious suspect was chlorogenic acid, which is present in coffee in quantities as great as 5 percent (1). Upon electrophoresis, authentic chlorogenic acid gave two spots (or bands) as shown in figure 1, one of which corresponded exactly with spot number 15. The second band in synthetic chlorogenic acid is undoubtedly an isomer, probably a cis-trans isomer. Natural products often have only one such isomer.

CONFIRMATION OF CHLOROGENIC ACID AS A SUGAR COLORANT

Further confirmation that the material at spot number 15 was in fact chlorogenic acid was obtained by thin layer chromatography. Each thin layer confirmation was double checked by eluting the spots with isopropanol and reconfirming the desired spot number by high voltage paper electrophoresis.

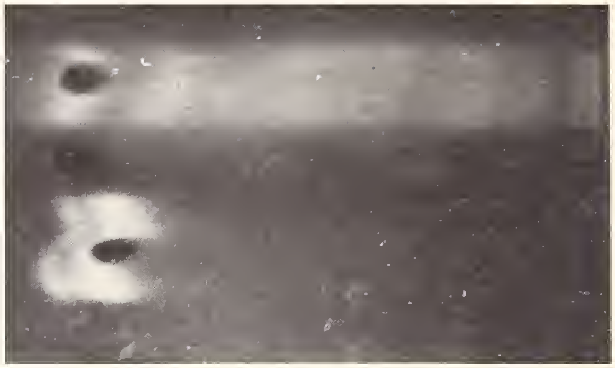


Figure 1. — FUPEG of cane leaf extract (upper) compared with chlorogenic acid (lower).

The results of the first thin layer test with chlorogenic acid were more than a little distressing. In a solvent mixture of methanol: benzene: acetic acid (2:11:1), the material at spot number 15 from either coffee or sugarcane remained at the origin, but authentic chlorogenic acid moved, with an R_f value of 0.10.

It is possible, however, that chlorogenic acid might be present in sugar as a salt. In thin layer chromatography, an acid and its salt are very likely to have different R_f values. This is in contrast to high voltage paper electrophoresis where the difference between an acid and its salt usually cannot be detected. The buffer used in electrophoresis effectively brings either the acid or its salt to the same degree of ionization, and hence with the same relative mobilities.

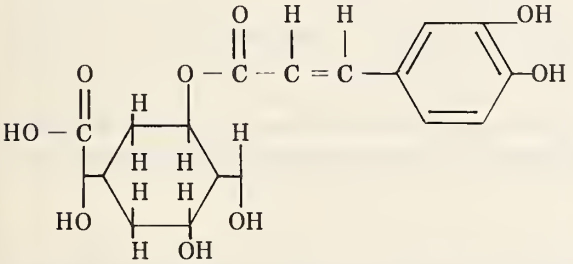
The material from coffee at spot number 15 was transformed into the acid form by acidifying a water solution and then extracting with ethyl acetate. Thin layer chromatography now showed both chlorogenic acid and the coffee material at spot number 15 to have an R_f of 0.10. Sugarcane material at spot number 15 behaved in a similar manner.

It was necessary in the thin layer chromatography to use calcium sulfate free silica gel because calcium sulfate was sometimes found to interfere with the elution of the material. Since many of the sugar colorant materials have low solubilities in nonpolar solvents, it was necessary to employ more polar solvents such as methanol and isopropanol to elute the compounds. Calcium sulfate has some solubility in these solvents and will, therefore, contaminate the recovered materials. It was also found that the presence of calcium sulfate in the silica gel sometimes interferes with movement of the colorant on a plate. As an extreme example, 4-hydroxy-3,5-dimethoxycinnamic acid was found to have an R_f value of zero when calcium sulfate was present and of 0.34 when calcium sulfate was not present in the silica gel (solvent system toluene: chloroform: acetone (8:5:7)). The reason for this is not known but since calcium salts play an important role in sugar refining, this phenomenon should be studied further for possible use in removing these colorants.

Using plates coated with calcium sulfate-free silica gel, two additional solvent systems were tried. A mixture of methanol: benzene: acetic acid (3:5:1) gave an R_f of 0.60 for the material at spot number 15 derived from coffee, the material at spot number 15 from cane leaf extract, and authentic chlorogenic acid.

In addition, in a solvent system of methanol and acetic acid (1:2), the R_f of chlorogenic acid and that of the material at spot number 15, regardless of the source, was 0.77. This made four chromatographic type confirmations: one high voltage paper electrophoresis and three very different thin layer systems. This was considered to be sufficient evidence for the confirmation of chlorogenic acid as a sugar colorant.

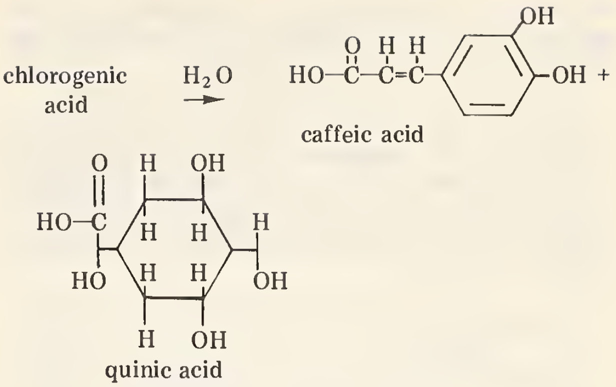
Chlorogenic acid has the structural formula:



It is a colorless, crystalline material that acquires an orange color in alkaline solution. At room temperature its solubility in water is about 4 percent, and is much higher in hot water. In neutral solution it will pick up oxygen and form green colored pigments. In alkaline medium and in the presence of enzymes it will react with oxygen to form a brown pigment. In the presence of iron it forms a green colored solution (2). It has a maximum absorption peak at 322.5 nm. with a molar absorptivity of 18,500 (1).

CAFFEIC ACID
(3,4-dihydroxycinnamic acid)

Chlorogenic acid upon hydrolysis yields both caffeic and quinic acids.



Therefore, as soon as it was certain that chlorogenic acid was a component of sugarcane, both caffeic and quinic acids were suspected as cane constituents. Caffeic acid, a yellow-colored compound, is fluorescent. Quinic acid does not fluoresce and, since the detection method at present in use is fluorescence, is beyond the scope of this report.

A high voltage electrophoresis comparison between caffeic acid and an ethyl acetate extract of cane leaf (6) is shown in figure 2 where two bands are seen for caffeic acid. These are apparently the cis- and trans-forms of the compound. The two bands of caffeic acid correspond to spot numbers 22 and 23. The colorant at spot number 23, one of the isomers of caffeic acid, was found to be present in liquor off nearly spent bone char but was not found in granulated sugar (6).

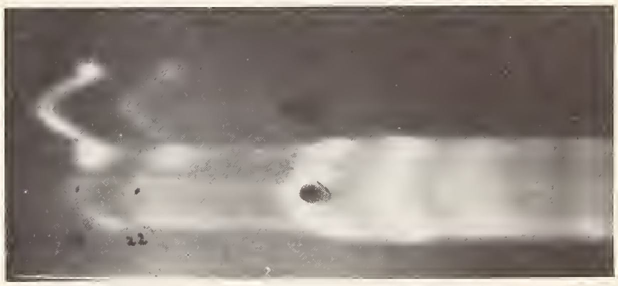


Figure 2. — FUPEG of caffeic acid (upper) compared with cane leaf extract (lower).

Long before spot number 15 had been identified, it was found (6) to hydrolyze to yield colorants located at spot numbers 3, 21, and 22. At that time, however, only a trace quantity of the material at spot number 15 was available and it was difficult to determine the spot numbers exactly. It appears now that caffeic acid, which in fact will be formed when chlorogenic acid hydrolyzes, is represented by spot numbers 22 and 23, not 21 and 22. Quinic acid, the other hydrolytic product, does not fluoresce so it cannot be spot number 3.

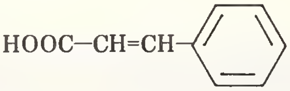
In a manner similar to that used for the identification of chlorogenic acid, the presence of caffeic acid was further confirmed by thin layer chromatography. The solvent systems used and the corresponding R_f values for caffeic acid are listed below.

Solvent system:	R_f
methanol: benzene: acetic acid (2:11:1)	0.27
benzene: acetic acid: dioxane (22:1:6)	.18
methanol: acetic acid (1:2)	.81

Caffeic acid is a yellow crystalline solid. It forms a light yellow solution in water, which becomes orange upon addition of alkali, and green upon addition of ferric chloride. The colorant has its principal absorption peak at 326 nm. with a molar absorptivity of 18,600 in ethanol (12).

CINNAMIC ACID

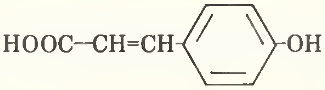
The finding of chlorogenic and caffeic acids as colorants in sugarcane led to a search for the parent compound, cinnamic acid, and other derivatives. Cinnamic acid



was not found.

p-HYDROXYCINNAMIC ACID
(p-coumaric acid)

A cinnamic acid derivative which was found is p-hydroxycinnamic acid,



Two blue fluorescing spots were observed in the FUPEG for p-hydroxycinnamic acid and these represent the cis- and trans- forms of the compound. Their $M_{HMF\text{-}PIC}$ values were 1.13 and 1.18, corresponding to spot numbers 20 and 21.

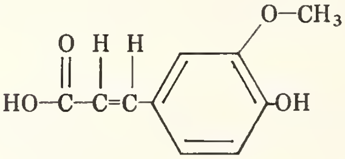
Spot number 20 has been found in granulated sugars. Spot number 21 was found in syrup off regenerated granular carbon but was not found in granulated sugar (6).

The presence of p-hydroxycinnamic acid was confirmed in a manner similar to that described for chlorogenic and caffeic acids. The solvent systems used and the corresponding R_f values are listed below:

Solvent System:	R_f
benzene: acetic acid: dioxane (22:1:6)	0.37
methanol: benzene: acetic acid (2:11:1)	.53
toluene: chloroform: acetone (8:5:7)	.43

The compound is a yellow crystalline substance, only slightly soluble in water and much more so in alkaline solution. Its sodium salt is yellow. With ferric chloride it gives a dark golden brown color. The trans-form has an absorption maximum at 311 nm. The cis-form has an absorption maximum at 302 nm. (5). Jurd (12) reports the principal absorption peak for p-hydroxycinnamic acid to be 312 nm. with a molecular absorptivity of 22,900 in ethanol.

4-HYDROXY-3-METHOXYCINNAMIC ACID
(ferulic acid)



Ferulic acid is the 3-methoxy derivative of caffeic acid, which it closely resembles in structure. It is found in many plant species (11a).

Electrophoresis gives two bands for 4-hydroxy-3-methoxycinnamic acid which are obviously the cis- and trans- forms. One band having an $M_{HMF\text{-}PIC}$ value of 0.97 coincides with spot number 14. Spot number 14 was present in granulated sugar (6). The second band has an $M_{HMF\text{-}PIC}$ value of 1.08 and coincides with spot number 15.6.

Using the method previously described, the presence of 4-hydroxy-3-methoxycinnamic acid was confirmed by thin layer chromatography. The solvent system used and the corresponding R_f values are listed below:

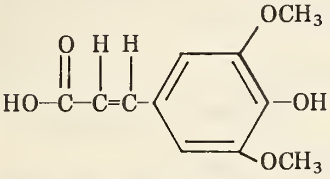
Solvent System:	R_f
benzene: acetic acid: dioxane (22:1:6)	0.54
methanol: benezene: acetic acid (2:11:1)	.69
toluene: chloroform: acetone (8:5:7)	.38

The trans- form of the acid is a white solid with a melting point of 174°C. Its absorption maxima in ethanol are 236 nm. and 322 nm. (10). Jurd (12) reports the principal maximum to be at 323 nm. with a molar absorptivity of 16,600.

The cis- form is a yellow oil with an absorption maximum in alcohol at 317 nm. (5).

The compound 4-hydroxy-3-methoxycinnamic acid dissolves in aqueous alkali to give a yellow colored solution (3).

4-HYDROXY-3,5-DIMETHOXYCINNAMIC ACID (sinapic acid)



This material is frequently found in plants (11a).

A comparison between 4-hydroxy-3,5-dimethoxycinnamic acid and cane leaf extract is shown in figure 3. As with the other cinnamic acids, this acid had two bands representing the cis- and trans- forms. The $M_{HMF\text{-}PIC}$ of the two bands are 0.73 and 0.92. The band having $M_{HMF\text{-}PIC} = 0.92$ corresponds to spot number 13, which appears in refined sugar (6). The second band, however, with $M_{HMF\text{-}PIC} = 0.73$ does not correspond well with any spot number. On the FUPEG it tends to coincide with spot number 12, but spot number 12 has an orange-yellow fluorescence, while the corresponding band from 4-hydroxy-3,5-dimethoxycinnamic acid has a blue fluorescence. Throughout this entire study the less mobile band could not be clearly observed in the sugar extract.

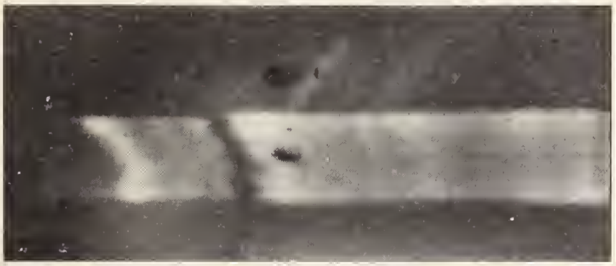


Figure 3. — FUPEG of 4-hydroxy-3,5-dimethoxycinnamic acid (upper) and cane leaf extract (lower).

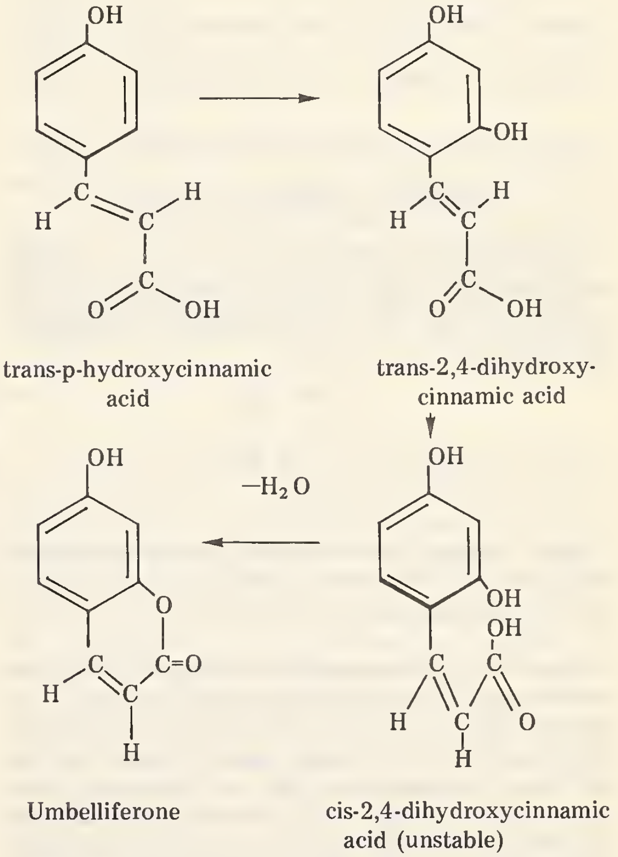
As before, further confirmation was made by thin layer chromatography. The solvent system employed and the corresponding R_f values for 4-hydroxy-3,5-dimethoxycinnamic acid are listed below:

Solvent System:	R_f
toluene: chloroform: acetone (8:5:7)	0.34
toluene: ethyl formate: formic acid (5:4:1)	.42
benzene: acetic acid: dioxane (22:1:6)	.41
methanol: benzene: acetic acid (2:11:1)	.50

4-Hydroxy-3,5-dimethoxycinnamic acid is an almost colorless crystalline solid. It dissolves in alkali to give a light yellow solution and forms a dark red color in the presence of ferric chloride (4).

UMBELLIFERONE
(7-hydroxycoumarin)

Umbelliferone can be synthesized (11b) by plants from p-hydroxycinnamic acid as follows:



trans-p-hydroxycinnamic acid

trans-2,4-dihydroxy-cinnamic acid

Umbelliferone

cis-2,4-dihydroxycinnamic acid (unstable)

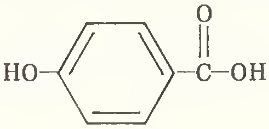
Since p-hydroxycinnamic acid had already been found in sugarcane, the presence of umbelliferone was also suspected, and confirmed by high voltage paper electrophoresis. The $M_{HMF\text{-}PIC}$ value for umbelliferone was 0.82, corresponding to spot number 11.5. Spot number 11.5 is found in liquor off nearly spent granular carbon but is not present in granulated sugar (6). The spot fluoresced blue when excited by both 365 nm. and 253 nm., its fluorescence being much more intense when excited by the longer wavelength. Originally this spot was reported to have a purple fluorescence when excited by 365 nm, and no fluorescence at all when excited by 253 nm. Since the FUPEG of cane leaf extract contains many colorants, some of them superimposed one upon the other, it is probable that in some sugars other colorants may be present at this spot. However, in some instances, spot number 11.5 does have an intense blue fluorescence.

Further confirmation was obtained by thin layer chromatography similar to that described previously. The solvent system used, and the corresponding R_f values of umbelliferone, are listed below:

Solvent System:	R_f
formic acid: ethyl acetate: methyl ethyl ketone: water (1:5:3:1)	0.96
ethyl acetate: methyl ethyl ketone (5:3)	.73
methanol: benzene: acetic acid (3:7:1)	.75
toluene: ethyl formate: formic acid (5:8:6)	.68

p-HYDROXYBENZOIC ACID

Hydroxybenzoic acids are usually found in plants containing lignin (11a). Since the sugarcane plant does contain lignin, the presence of this type of compound was suspected.



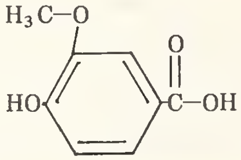
High voltage paper electrophoresis indicated the presence of p-hydroxybenzoic acid in cane leaf extract. It had an $M_{MHMF\text{-}PIC}$ value of 1.42.

Upon initial exposure the spot had a faint blue fluorescence at both excitation wavelengths. After ten minutes, however, it lost its fluorescence at excitation wavelength 365 nm. At an excitation wavelength of 253 nm., the spot also lost its fluorescence and quenched the background fluorescence of the paper (the spot appeared black). Since this spot had not been observed during the original survey (6), it was given the new number 22.1 in the numbering system.

The presence of p-hydroxybenzoic acid in cane leaf extract was confirmed by thin layer chromatography. The solvent system and the corresponding R_f values of p-hydroxybenzoic acid are listed below:

Solvent System:	R_f
benzene: acetic acid: dioxane (22:1:6)	0.39
methanol: benzene: acetic acid (2:11:1)	.46
toluene: ethyl formate: formic acid (5:4:1)	.41

4-HYDROXY-3-METHOXYBENZOIC ACID (vanillic acid)

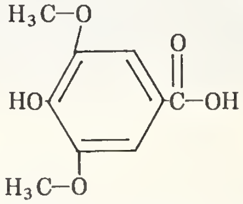


Upon electrophoresis, 4-hydroxy-3-methoxybenzoic acid had an $M_{HMF\text{-}PIC}$ value of 1.28. It does not fluoresce at an excitation wavelength of 365 nm., but does quench the background fluorescence of the paper at an excitation wavelength of 253 nm. It has been assigned the new number 21.1 in the numbering system, since this spot had not been observed during the original survey (6).

Its presence was confirmed by thin layer chromatography. The data are listed below:

Solvent System	R_f
benzene: acetic acid: dioxane (22:1:6)	0.42
methanol: benzene: acetic acid (2:11:1)	0.57
toluene: ethyl formate: formic acid (5:4:1)	0.42

4-HYDROXY-3,5-DIMETHOXYBENZOIC ACID (syringic acid)



High voltage paper electrophoresis of 4-hydroxy-3,5-dimethoxybenzoic acid showed it to have a $M_{HMF\text{-}PIC}$ value of 1.07 and to be located at spot number 17. Under an excitation wavelength of 253 nm. it appeared to have a blue fluorescence at first, but shortly afterwards showed a quenching of the background fluorescence of the paper. It is not observable under an excitation wavelength of 365 nm.

Originally it was reported (6) that colorant number 17 appeared black when excited by either 365 nm. or 253 nm. It is clear now that the black color originally observed when excited by 365 nm. was caused by another, as yet unknown compound located at the same place.

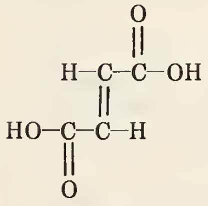
Spot number 17 was found in liquor off nearly spent granular carbon. The compound 4-hydroxy-3,5-dimethoxybenzoic acid had already been found in cane juice in 1959 (18).

The thin layer chromatographic data used to determine its presence in cane leaf extract is shown below:

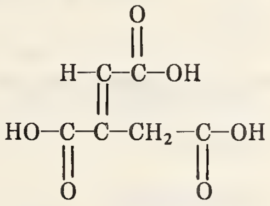
Solvent System:	R_f
benzene: acetic acid: dioxane (22:1:6)	0.49
toluene: ethyl formate: formic acid (5:4:1)	.40
benzene: acetic acid (5:1)	.39

UNSATURATED POLYCARBOXYLIC ACIDS

It is already known that both fumaric (16, 17) and aconitic (14) acids are present in cane sugar.



Fumaric Acid



Aconitic Acid

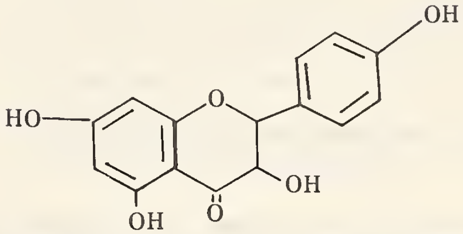
High voltage paper electrophoresis revealed that both these compounds are located at spot number 28 in the numbering system. Both quench the background fluorescence of the paper at an excitation wavelength of 253 nm. and are not observable at an excitation wavelength of 365 nm. Both have $M_{HMF\text{-}PIC}$ values of 2.24. Since a spot at spot number 28 appeared in granulated sugar (6), either one or both of these two compounds may be present in refined sugar.

Although fumaric and aconitic acids are not separated by high voltage electrophoresis under the conditions used, separation can be brought about by thin layer chromatography on silica gel G.

The data are shown below:

Solvent System	R_f Fumaric Acid	R_f Aconitic Acid
methanol: benzene: acetic acid (2:11:1)	0.28	0.17
benzene: acetic acid: dioxane (22:1:6)	.15	.05
toluene: formic acid: methyl formate (5:1:4)	.41	.28

KAEMPFEROL



The flavonoid, kaempferol, is bright yellow, with a melting point of 276°-278°C. (15), and absorption maxima at 265 and 365 nm. (13, 15). It is only slightly soluble in water, but is soluble in hot alcohol, ether and alkalies.

Upon electrophoresis kaempferol moves very little and is located at spot number 1, which was present in liquor off freshly regenerated granular carbon. Its low mobility makes high voltage paper electrophoresis a poor media for identifying this compound. In chromatography it is usually desirable to have a compound move some distance from the origin. It was, therefore, necessary to find another, more suitable method to study the compound.

Gas chromatography was found to be most helpful. The procedure used for the identification of kaempferol was similar to that described for the other compounds, except that gas chromatography replaced high voltage paper electrophoresis as a method of monitoring the thin layer chromatography separation. For kaempferol, it is necessary to silylate the compound. The dried, lyophilized sample was dissolved in anhydrous pyridine and silylated by adding hexamethyldisilazane and trimethylchlorosilane. A Hewlett-Packard chromatograph Model 5750 with a column of 10 percent OV-1 (silicone gum rubber), on Chromosorb P, 6 feet long, 1/8 inch diameter was used. The column temperature was 270°C. Retention time was 15 minutes. Regardless of the solvent system used for thin layer chromatography, the eluate always displayed a peak on the gas chromatograph that had the same retention time as authentic kaempferol.

The solvent system used for thin layer chromatography and the resultant R_f values obtained for kaempferol are given in the following table:

Solvent System:	R_f
chloroform: formic acid: ethyl acetate (5:1:4)	0.56
toluene: ethyl formate: formic acid (5:4:1)	.41
benzene: formic acid: ethyl acetate (9:4:5)	.60

RELATIONSHIP OF FLAVONES TO CINNAMIC ACIDS

An interesting fact reported by Geissman and Harborne (7) is that albino mutants of the snapdragon plant accumulate esters of p-coumaric and caffeic acids instead of the related flavones found in colored genotypes. Albino forms of the garden snapdragon are distinguished from nonalbino "white" flowers in that the latter are actually a cream or ivory color and possess traces of pigments on lips and throat; the albinos are a chalk-white color and possess no visible yellow pigmentation.

In studying the albino mutant, Geissman and Harborne worked with an extreme case. Possibly even in nonalbino plants, including sugarcane, there is an inverse relationship between flavones and cinnamic acids. The relative quantities of each could depend upon both genetic and environmental factors.

A raw sugar could have a high concentration of cinnamic acids and a relatively low concentration of flavones. Since most cinnamic acids and their derivatives are light yellow in color, and flavones are darker yellow in color, a raw sugar of this nature would appear to be light yellow in color and lead the refiner to believe that it would be easy to decolorize. If what is indicated in this report is true, namely that cinnamic acids are not readily removed by currently known refining processes, then the refiner would find the sugar difficult to decolorize. This may explain why a light colored raw sugar can sometimes be so troublesome to refine. The development of analytical procedures for the determination of cinnamic acids and flavones in sugar may provide a means for anticipating this problem.

SUMMARY

A list of the colorants found and their locations in the spot numbering system is given below.

Compound	Spot Number
1. Kaempferol	1
2. Umbelliferone	11.5
3. 4-Hydroxy-3,5-dimethoxycinnamic acid	13, 12
4. 4-Hydroxy-3-methoxycinnamic acid	14, 15.6
5. Chlorogenic acid	15
6. p-Hydroxycinnamic acid	20, 21
7. Caffeic acid	22, 23

Several additional compounds, which are not colored, have also been found. A list of these compounds and their spot numbers are given below.

Compound	Spot Number
1. 4-Hydroxy-3,5-dimethoxybenzoic acid	17
2. 4-Hydroxy-3-methoxybenzoic acid	21.1
3. p-Hydroxybenzoic acid	22.1
4. Fumaric acid	28
5. Aconitic acid	28

In general, kaempferol and probably a great many other flavonoids are located at the low numbered spots. Some of the flavonoid glycosides, however, are probably located at higher spot numbers. The cinnamic and benzoic acids and their derivatives can be found in the central part of the FUPEG ranging in spot numbers from 11.1 to 23. At the far end of the FUPEG fumaric and aconitic acids are located at spot number 28. It is strongly suspected that a number of other unsaturated polycarboxylic acids are located in this region of the FUPEG.

This is a major advancement: for the first time, specific compounds have been identified as the colorants in cane sugar. It is not claimed or even suggested that all the colorants in cane sugar have been identified. Neither is it claimed that the colorants present in the largest amount, nor those most difficult to remove, have been identified.

We have identified several cane pigments as colorants that do definitely elude all the present refining processes and get through even to the refined sugar.

However, mere identification of these materials is not enough. The next step is to devise analytical methods to measure the quantities of these materials present at various refining stages. Further study of their optical and chemical properties should lead to the most economical way to get rid of them.

ACKNOWLEDGEMENT

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DISCUSSION

F. M. WILLIAMS: Would you hazard a guess as to how best these colorants could be removed, whether by activated carbon, by ion exchange, or by some other means?

L. FARBER: It is still premature to venture a guess of that nature. This paper is only a brief summary: we have additional evidence too detailed to present now, which indicates that some colorants such as chlorogenic acid may exist in complex forms, or salt forms. Until we know specifically what these forms are, it's too early to determine the best method of removal. The compounds identified so far are acidic in nature and an anion exchanger should obviously take out all of them. However, we don't yet know the quantities involved — that's the next step, after we identify the colorants. Some are probably present in one raw that are not present in others, or present in different quantities. I suspect that the bright yellow flavonols from our original preliminary survey are not as important as these light yellow substituted cinnamic acids, which are more difficult to get out. That's why sometimes a refiner may find a great deal more trouble with a light yellow raw than with one of a dark yellow or intense yellow color. But this is purely conjecture.

D. E. TIPPENS: You are establishing the stability of chlorogenic acid through reflux. At what temperature and pressure did you reflux?

L. FARBER: In water, around 100°C, at atmospheric pressure.

D. E. TIPPENS: Did you do this to all of these colorants that you've identified? Is there a possibility that they might be chemical intermediates in a reaction?

L. FARBER: We found many of them in the refined granulated sugar.

D. E. TIPPENS: Have you, or do you know of, a method of extracting and identifying these by the classical organic methods?

L. FARBER: We will avoid isolation if possible, and identify by chromatographic methods, because there are so many compounds to identify. Although twelve compounds may look impressive, I believe we've only scratched the surface. However, a particular compound for which there is no chromatographic standard of reference will have to be isolated. One such case is component number 10, which still remains to be identified.

We have isolated component number 10, a bright yellow compound, from ion exchange washings obtained from a refinery. From preliminary investigations, we knew ion exchange washings to be especially rich in number 10. The washings were saturated with sodium chloride and extracted with isopropanol. Number 10 was then isolated from the extract by thin layer chromatography. We plan to identify this compound later, after studying more of the aglycons. We strongly suspect that 10 is a glycoside. If we know more about these flavonols without sugars attached (aglycons), we will have more insight into the glycosides. We are also considering the possibility, in some cases, of isolating and purifying additional compounds for characterization.

L. A. ANHAISER: I'd like to ask a question on the base test that you make on raw sugars or raw juices. Has any attempt been made to keep track of the different varieties or sources, and to see if the colors are the same from different varieties or from different places? Are all the colorants in all the raws?

L. FARBER: We will investigate this when we have more information about the identity of these colorants. We want to determine which colorants are the most troublesome to remove. Our preliminary survey gave us some indication of this. Now we're trying to find out more about what the compounds are, and then we will make a survey of their origins.

J. T. RAMAGE: How do the colorants in cane show up against those in beet?

L. FARBER: We once tried an extract of beet molasses on electrophoresis, and the pattern is not the same — there are different colorants there. It's a different plant, and you would expect a different set of impurities. We really didn't go into detail to see if any spots matched, but it's definitely not the same.

P. F. MEADS: Do all of these colorants come from the plant or could some come from degradation of the sugar?

L. FARBER: All of these that we studied came from the plant, from the leaf of the sugarcane, which we extracted by boiling in water, concentrating and acidifying, and extracting with ethyl acetate. We find the same colorants also when we go through this procedure with raw sugars.

P. F. MEADS: I think Dr. Farber should be complimented on this work. It should be noted that there are two ways of approaching this problem. We are approaching it differently from Dr. Farber. We are trying to collect enough of the various fractions obtained, say by gel filtration, to determine whether a particular fraction has an adverse effect on the refining process. For instance, is it difficult to absorb on bone char, or does the color boil into the grain? If the fraction doesn't bother us, let's forget about it and center our attention on those fractions that give us problems. We will further divide these adverse fractions and work on the adverse subfractions. From a refiner's standpoint, you may be spinning your wheels taking the time to identify colorants that don't give you any problem. So we're taking the other approach.

L. FARBER: We oriented our studies toward those colorants that do appear in the final product. Number 15, the colorant first identified, does appear in the final granulated sugar. Those colorants are the toughest to remove.

P. F. MEADS: Maybe they are present in large quantities at the start, and a large proportion of them is removed in the process. Maybe if you could reduce the starting quantity, the amount left after refining would not be troublesome.

F. G. CARPENTER: There's a philosophy here, of course. I believe you'll find there are three laboratories working on colorants. Ken Parker at Tate and Lyle is basing his separation on ion exchange, you are separating yours on gel filtration, and we're separating ours by high-voltage paper electrophoresis. So we are looking at the same thing: which colorants are in the final sugar. Our approaches, however, are different. Actually this is healthy. It's worthwhile to go after things from different angles. Eventually, if we're highly successful, we should all end up finding the same compounds. However, because we're going in different directions, hopefully we'll help out each other and won't have to duplicate work.

P. F. MEADS: I agree. It's much better that we use different approaches; otherwise we're simply duplicating work.

F. G. CARPENTER: We are looking primarily at the colorants which we find in granulated sugar. Number 15 is the only one which I have found in every sample of sugar I've ever looked at, even in first strike granulated. We took 10 pounds of first strike granulated, and precipitated out the sucrose by adding alcohol, then took the remaining pale yellow solution, and twice repeated the procedure. Next, we put the final product — one half drop of pale yellow fluid — on electrophoresis, and found number 15. It is there in very small quantity, but it is the only colorant found in every sample of sugar ever tested.

F. M. WILLIAMS: Did this spot 15 show up also in liquid sugar?

F. G. CARPENTER: Yes, it's in liquid sugar. The best sugar is undoubtedly first strike granulated; the liquid sugar is not that good.

R. E. ANDERSON: To give you a little cross fertilization from a different field: there's been a problem in the water conditioning industry for a number of years with colored materials in surface waters. These tend to foul the quaternary resins used in water conditioning. In the last few years a number of these particular materials have been identified. They are believed to come from leaf molds, from runoff water from forests, etc. It's very interesting that several of these compounds turn out to be the very same compounds you're talking about, the phenolic carboxylic acids.

F. G. CARPENTER: That is not really too surprising; in the sugar mill there are leaf products present. The amazing thing is that the leaf pigments survive all the processing. A good many years ago, when I first started in this business, plant pigments were considered unimportant because they were all too fragile and would certainly be decomposed in the very first few stages of processing. But now we have found that the one colorant that is always in even the best granulated is in fact a plant pigment.

F. M. WILLIAMS: You said that the green coffee bean has chlorogenic acid to an extent of about 5 percent. After roasting, this has shrunk to 3 percent. Generally when we roast a carbon, we start with a coal of 1 percent ash and end up with an activated carbon of 8 percent ash. As the weight goes down, water and organics, etc. are driven off, and the ash content as a percent by weight increases. Now, is this a heat sensitive acid which could be driven off by heat?

L. FARBER: If you heat it high enough, it will decompose. Then you'll have other things to worry about — oxidation products, quinones, and other products. I don't think you'll decolorize a sugar solution by heating it.

E. NABORNEY: Do all these compounds have a common functional group on which you could use some type of reaction to remove them?

L. FARBER: All of them seem to have a phenolic group. Some of them are carboxylic acids, so the anion exchangers should get them. But this question is probably premature because, as I mentioned earlier, there may be complexes.

S. B. SMITH: You mentioned that you haven't quantitized this situation yet, but it seems as though the molecular weights that you're looking at are rather low compared to what we think we've been adsorbing on carbon. Now I wonder if, for the compounds so far identified, you have any idea what proportion of the total colored material this might represent, because there obviously are some higher molecular weight things involved too.

L. FARBER: We do not know proportions yet, but the question of which molecular weight range components are most difficult to remove is an important one.

F. G. CARPENTER: We have not yet quantitized because, although we could, of course, do this for compounds already known, we plan to wait until most of the components are identified, and we can determine the best ways to measure them.

S. B. SMITH: I might point out an analogy here — the surface waters that Dr. Anderson mentioned have been studied by collecting the contaminants on carbon. They use columns of carbon as a standard test in the water field, and then elute the contaminants — colored materials or flavor producing materials, etc. — by extracting with chloroform. I wonder if this technique might not constitute a good way of concentrating some of these things for future identification — take a saturated carbon or a char and then try to get the material back off by solvent extraction?

F. G. CARPENTER: There are a thousand ways of separating these things — you can collect them on an ion-exchanger, a carbon, a piece of paper, an old rusty pipe or anything else you want and then you've got to get them back off. And the one place that they come off from the hardest is the carbon. Take a look at the color balance over your carbon someday and you will discover that 99 percent or so of the color is collected out of the sugar. How much of that color reappears in the wash water? Virtually none. You have to burn it off the carbon. From an ion-exchanger, you can wash off a good percentage of the color, but even there you still can't recover it all.

Now, when you rely upon something like that to collect colorant quantitatively, you are complicating matters because of the strong chemical methods necessary to remove the colorant. For example, Zaorska,[1] in Poland, collected colorant on carbon and removed it with pyridine. Pyridine is almost certain to change the colorant molecular structures. You've got to treat these compounds gently when you get them separated from the sugar, as Ken Parker said this morning, or you completely ruin them. There is even a school of thought which says that merely the removal of the colorants from sucrose will change their nature. We do have a problem here, but we are working on it.

C. FORMECK: Do you find chlorogenic acid in water white liquors?

L. FARBER: Yes. It was found in all final liquors and granulated sugars that we have tested so far. We will continue to check more water white liquors.

F. G. CARPENTER: If you make the very whitest of sugars alkaline, you will get a yellow color. The color compounds are there.

C. FORMECK: The amount remaining in the sugar would depend on the amount of carbon used to decolorize the liquor.

F. G. CARPENTER: True, you can make extra pure, chemically pure, sucrose by repeated use of a lot of carbon, and eventually end up with no chlorogenic acid. I suspect, however, that chlorogenic acid is one of the last things to be removed.

D. E. TIPPENS: Did sugar refined by carbonatation also contain chlorogenic acid?

F. G. CARPENTER: Yes, it did.

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[1] Zaorska, H., 1966. Influence of color substances on the color of sugar. Gaz Cukr. 74: 157-62 (Sugar Ind. Abstracts 1967:76)

FLUORESCENCE OF SUGARS

by

James H. Wall and Frank G. Carpenter
Southern Marketing and Nutrition Research Division
New Orleans, La.

(Presented by Frank G. Carpenter)

ABSTRACT

A preliminary survey of fluorescence in sugar shows that it could possibly replace the color measurement. It is more sensitive than color in the low region and, perhaps, more informative. It is worthy of further study.

INTRODUCTION

Although sucrose and invert sugars do not fluoresce, commercial sugars always show at least some slight fluorescence. This is undoubtedly due to trace constituents, and there is a possibility that fluorescence might be a useful way to measure these trace constituents. Heretofore, fluorescence has been largely ignored because the intensity of fluorescent light is very weak, and, therefore, very expensive photomultiplier tube type instrumentation was required. With the development in recent years of cadmium sulphide photodetectors, the cost of measuring low levels of light has been reduced more than one hundred fold, which makes fluorescence more interesting.

Since there is no record of the fluorescence characteristics of the whole gamut of commercial sugars, the following preliminary survey was undertaken to define the problem. The objective was to see if fluorescence had any possibility of being a useful evaluation of commercial sugars.

FLUORESCENCE IN GENERAL

Fluorescence is defined as the absorption by matter of light at one wavelength and emission at a longer wavelength.[1] The theory of fluorescence is concerned with energy level shifts in electron orbits and molecular bonds, but this is not the subject of this report. Fluorescence can be used to confirm molecular structure, but again this is not the subject of this report. Fluorescence can be used to measure the amounts of fluorescing materials and this is the subject of this report.

Since fluorescence involves two wavelengths, the instrument requires two monochromators in an arrangement like figure 1. Fluorescence is emitted equally in all directions so the right-angle is not required, but it is convenient, and scattering is minimal in this direction.

Typical results obtained from such an instrument are shown in figure 2, which shows emission intensity I_f, plotted against emission wavelength E_m, at constant exciting wavelength E_x.

For emitted wavelengths less than the exciting wavelength, the emitted intensity is zero, because theoretically no fluorescence can occur at wavelengths below the exciting wavelength. In practice, this part of the curve is never examined. It is used only to check the zero of the instrument.

The large offscale peak at the exciting wavelength is ordinary scattering. This is not of interest in fluorescence measurements and is ignored. It is interesting to note at this point, however, that the intensity of the scattering is always many times less than the intensity of the incident beam. Here we see that the intensity of the fluorescence is many times smaller than the intensity of the scattering, which makes it very small indeed.

The sharp narrow Raman scattering peak comes from the water in the solution. The theory of Raman scattering is beyond the scope of this report. But, since water is always the solvent in sugar work, the Raman scattering of water will always be present. It is easily recognizable by its narrowness and by its location. It is always about 50 nanometers above the scattering peak. It, like the scattering peak, is ignored.

The broad fluorescence peak is the main object of interest in this report. In most of the remaining figures it is the only peak shown. A fourth peak will sometimes appear in instruments with grating monochromators. It is the first harmonic of the scattering peak, at twice the scattering wavelength.

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[1] For further details, consult any general text on fluorescence. The theory presented here was drawn largely from Fluorescence Assay in Biology and Medicine, S. Udenfriend, Academic Press, N. Y. 1962.

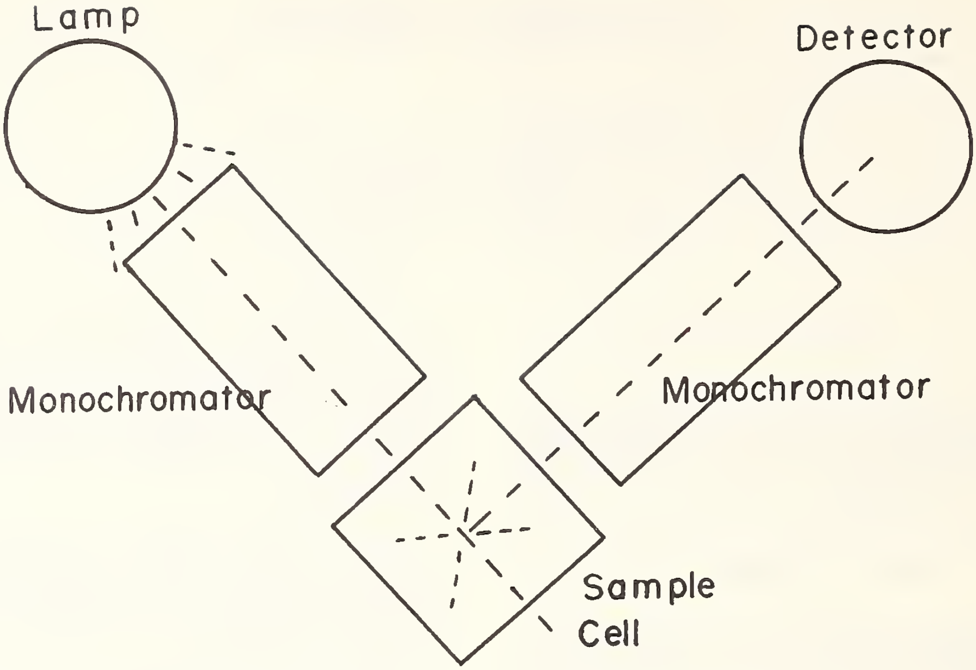

Figure 1. — Arrangement of typical fluorescence measuring instrument.

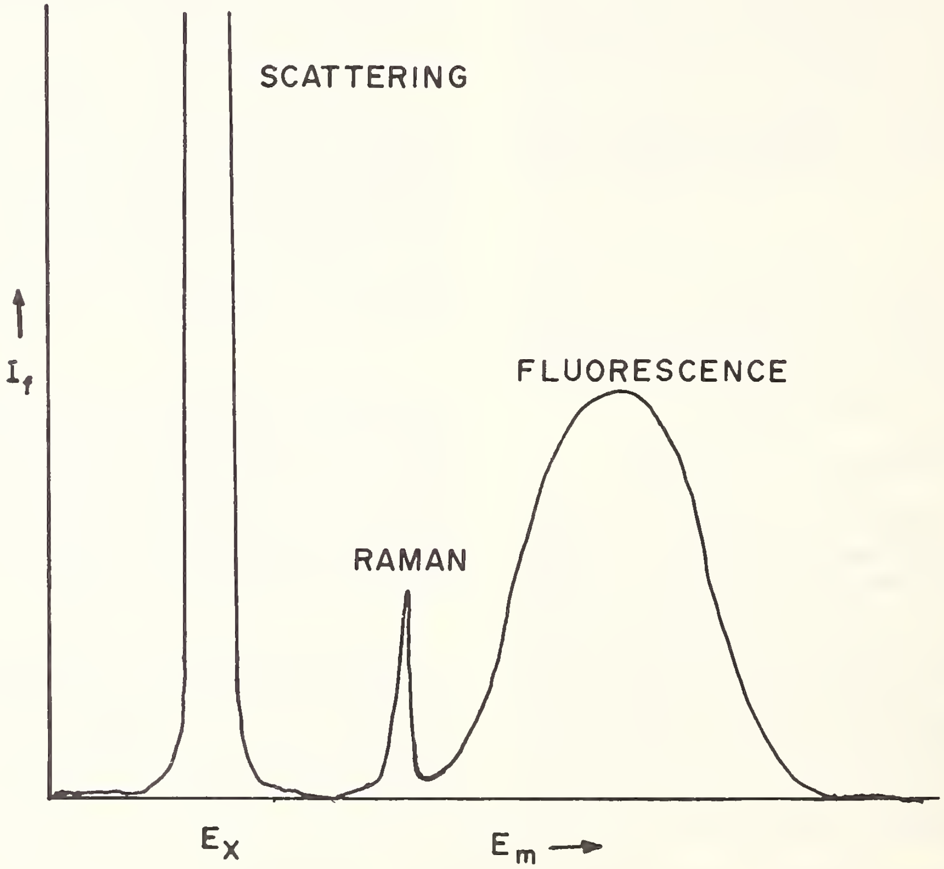

Figure 2. — Typical results obtained from fluorescence measurements.

Fluorescence requires three specifications for its description and, hence, can be called three-dimensional:

Excitation wavelength

Emission wavelength

Emission intensity

These three dimensions of fluorescence will be examined in turn.

FLUORESCENT INTENSITY

The primary mathematical expression describing the intensity of fluorescence is related to the definition of fluorescence which states that light is absorbed at one wavelength and emitted at another. The emitted, or fluorescent intensity, I_f, is proportional to the absorbed intensity, I_a, and using Q for the proportionality constant, the equation becomes:

$$I_f = I_a Q. \qquad (1)$$

Q is the quantum yield of fluorescence and can have a value ranging from zero up to one. A value of one means that all the energy absorbed is re-emitted as fluorescence. A few materials are known which have a quantum yield close to one, but most materials have a very low quantum yield. This is just a difficult way of saying that most materials do not fluoresce.

Quantum yields have not been tabulated for very many materials, and I_a is not usually measured, so equation 1 is not very useful as it stands. However, the light absorbed can be expressed as the difference between incident, I_o, and transmitted, I_t, light:

$$I_a = I_o - I_t. \qquad (2)$$

This assumes that no light is scattered, which is, of course, never the case. In practical fluorescence measurements, the solutions are dilute, optically clear, and have very little light scattering relative to absorption. Nevertheless, this assumption of zero scattering does constitute an error in the calculations. Equation 2 can be manipulated into the form:

$$I_a = I_o\left(1 - \frac{I_t}{I_o}\right). \qquad (3)$$

The term I_t/I_o is the transmittance, T, and equation 2 now becomes:

$$I_a = I_o(1-T) \qquad (4)$$

The transmittance is familiar to sugar chemists; they have been using it to measure color routinely. The familiar expression using transmittance is:

$$\frac{-\log T}{bc} = a, \qquad (5)$$

where b is the path length,
c is the concentration,
and a is a constant.

Equation 5 can be manipulated mathematically as follows:

$$-\log T = abc \qquad (6)$$

$$T = 10^{-abc} \qquad (7)$$

$$1-T = 1-10^{-abc} \qquad (8)$$

Equation 8 can be expanded in the exponential series and by taking only the first term:

$$1-T = 2.3\,abc \qquad (9)$$

In taking only the first term, the assumption is made that the factor abc is small, which is equivalent to assuming that the transmittance approaches one. For practical purposes, no error results from transmittances greater than 95 percent, and even at 80 percent transmittance the error from this assumption is not significant. This is also the practical range where fluorescence would normally be measured.

Inserting equations 9 and 4 into equation 1 gives

$$I_f = I_o\,\underline{2.3}\,\underline{a}\,\underline{b}\,c\,\underline{Q} \qquad (10)$$

In any one particular instrument and for any one fluorescent substance, the underlined factors are all constant and can be assembled into a single new constant, k, giving the more useful equation:

$$\underline{\underline{I_f = k\,I_o c.}} \qquad (11)$$

The assumptions that have gone into this equation are:

One particular instrument

One particular fluorescent substance

High transmittance (not dark-colored)

Low scattering (optically clear)

These are the conditions that would pertain for measuring the concentration of something by fluorescence, which is exactly the intended use in the sugar industry.

Note particularly that fluorescence intensity is directly proportional to the concentration of the fluorescent substance. This is quite in contrast to colorimetry where the -log function always appears.

FLUORESCENCE STANDARD

The simplicity of Equation 11 is deceiving because I_f and I_o are at different wavelengths and of quite different orders of magnitude. This brings up the instrumental problem of measurement.

They have to be measured with real photosensitive devices, not theoretical ones, and the response of real phototubes is wavelength dependent, and is linear only over a limited range.

This is in contrast to transmittance measurements, where I_o and I_t are at the same wavelength, so wavelength response is no factor; the intensity of the transmitted light ranges from that of the incident light downward by about 2 or 3 orders of magnitude. In fluorescence measurements the vast difference in intensity between the incident and fluorescent beams will usually be beyond the linear dynamic range of the phototube.

This can be neatly overcome by using a standard, and expressing the fluorescence, not in absolute units, but relative to the standard. This scheme also has the added advantage that instrumental geometric factors, which have not yet even been considered in this elementary discussion, are also cancelled out. For rather strong fluorescence, quinine sulfate is frequently used as a standard. For weak fluorescence in water solutions an alternative standard is the Raman peak of the water. We have chosen to use the Raman peak of water.

Equation 11 is repeated.

$$I_f = \underline{k}\, I_o c, \tag{11}$$

and then written for water:

$$I_w = \underline{k_w} I_o \underline{c_w}. \tag{12}$$

Upon dividing equation 11 by equation 12 the I_o's cancel out. Since in practice dilute solutions are used, the concentration of water, c_w, is a constant. Collecting all the underlined constants together into a new constant, F:

$$\frac{I_f}{I_w} = Fc. \tag{13}$$

$$\underline{\underline{F = \frac{I_f}{I_w c}}} \tag{14}$$

Equation 14 is the working equation, which says that the way to express fluorescence is in terms of fluorescent intensity relative to the Raman peak of water, and per unit concentration.

INSTRUMENT RESPONSE

The problem of wavelength dependence in phototube response still remains. In addition, the light source usually is not of equal intensity at all wavelengths, and the transmittance of the monochromators in the instrument can be wavelength dependent. Even the solutions being measured can have some wavelength dependence in their transmittances. All of these factors should be multiplied together and used to correct the measured fluorescence for these instrumental artifacts. Correcting instruments have been designed which automatically include all these wavelength dependent response factors and give a true corrected equal energy fluorescence spectrum, but these instruments are extremely expensive and temperamental. In this age of computers, it is probably easier to calculate the corrected fluorescence.

It is easier still to ignore the corrections for wavelength dependence altogether, and this is what is usually done. This type of measurement will depend upon the instrument used, but comparisons using the same instrument will be valid.

Since this was a preliminary survey, corrections were not made and all the results reported here are necessarily valid only for the instrument used, which was the Fluorispec Fluorescence Spectrophotometer, Model SF-1.[2]

Even though wavelength corrections were not made, it is of interest to evaluate the corrections just to see how much the reported results are in error. The biggest correction is the phototube response, R, which can be obtained from the manufacturer of the phototube.[3]

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[2] Manufactured by Baird-Atomic, Inc., 33 University Road, Cambridge, Mass. 02138, $8000.

[3] Manufactured by Radio Corporation of America, Electron Tube Div., Harrison, N. J.

This response factor for the 1P21 photomultiplier (S-4) is shown in figure 3. The other major correction is due to the source, S, which was a 150-watt xenon lamp.[4]

This intensity factor is also shown in figure 3. Other corrections are much smaller and are not considered in this preliminary work.

The total correction is the product of the two corrections as shown in figure 4. The relative response of the instrument was measured by putting a piece of white paper in the cell position at a 45° angle. These results are given as data points in figure 4, and are seen to agree reasonably well with the published average characteristics of lamp and phototube.

Figure 4 shows the relative response of the instrument. All measurements might have been corrected by dividing by this function, but they are not. Figure 4 shows that fluorescence at wavelengths above 600 nm. or below 300 nm. will not be detected by this instrument. The peak response of the instrument is at about 450 nm., which may be why many samples had a fluorescence peak in this region. The measured fluorescence peaks were much sharper than this response curve, so they were valid peaks, although the exact maximum would be shifted slightly by making the correction.

SOLVENTS

In any optical measurement the properties of the solvent must not interfere. The solvent in commercial

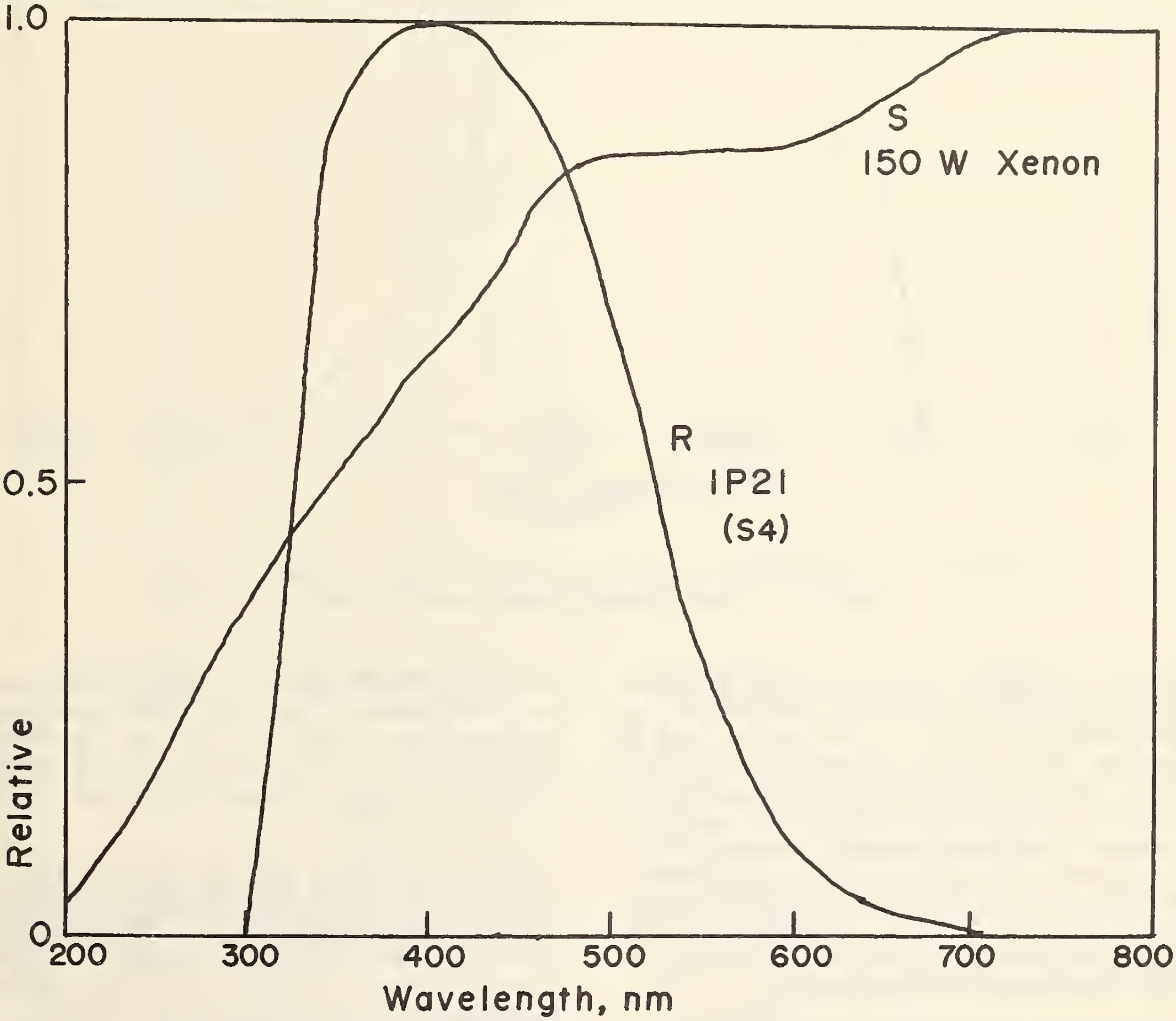

Figure 3. — Relative characteristics of light source and phototube.

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[4] Manufactured by Oriel Optics Corp., 1 Market St., Stamford, Conn. 06902.

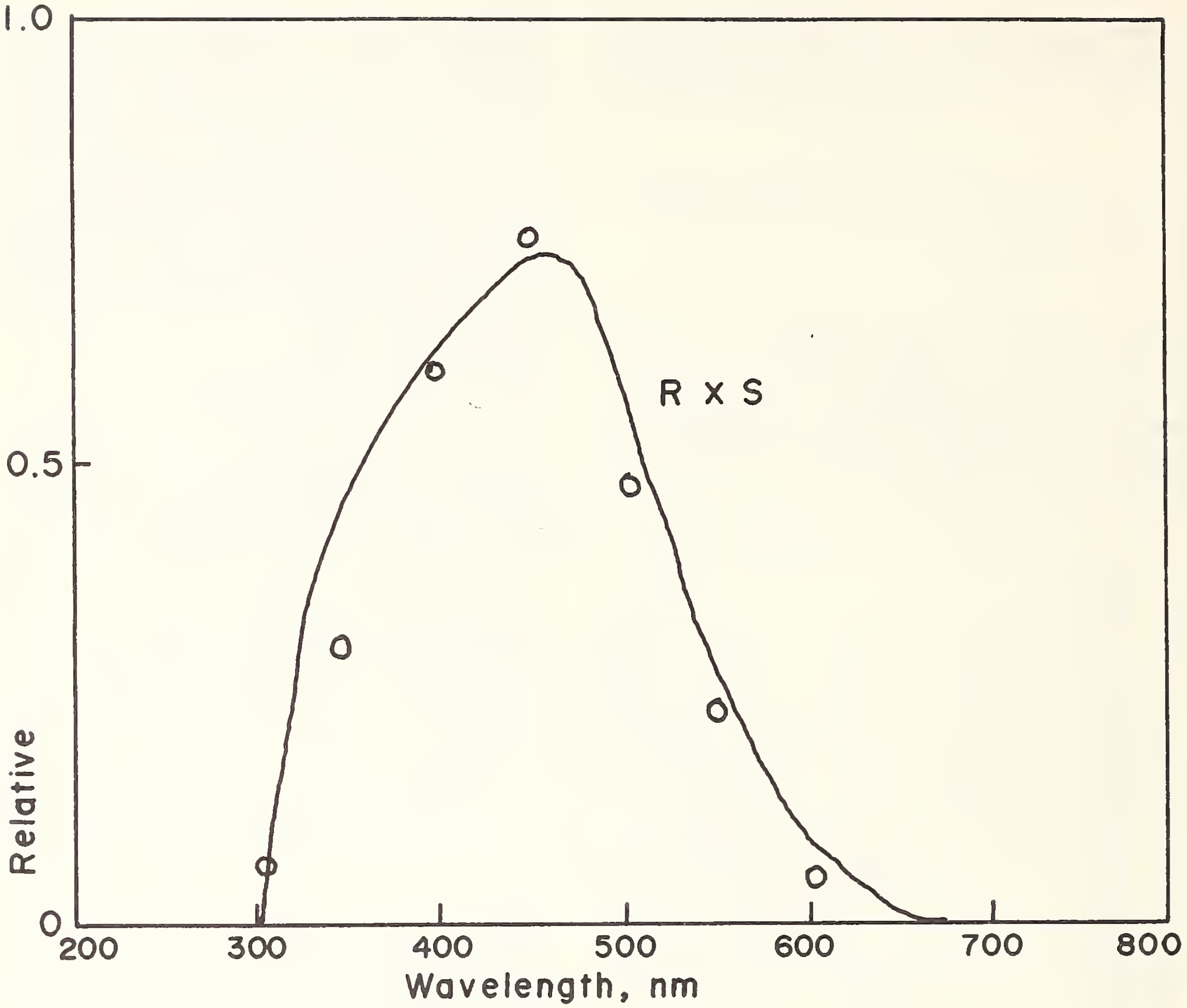

Figure 4. — Instrument response for the combination of light source and phototube used in this report. (These corrections were NOT used.)

sugar operations is a mixture of sucrose and water. Neither water nor sucrose has any fluorescence, but trace contamination in the usual supplies could be significant. The results of fluorescence measurements made on the pure materials are shown in figure 5. The excitation wavelength was 350 nm; and this figure shows the fluorescent intensity compared to the Raman peak of water as a function of the emitted wavelength. The sharp peaks are, of course, the Raman peak of water which was the standard. The dotted portions are estimations where the fluorescence was under the scattering and Raman peaks.

Figure 5 shows that the intensity of fluorescence in ordinary distilled water is only about 10 percent of the Raman peak. When this water was filtered through powdered activated carbon, the residual fluorescence was indistinguishable from zero. This means that powdered carbon does not add any fluorescing substances and water can easily be made "fluorescent pure". In fact, ordinary distilled water is pure enough for practical purposes.

It is well known that the purest sucrose is commercial first strike granulated, but by fluorescence this was of terrible purity, being way offscale on figure 5. However, after three filtrations through powdered activated carbon (Darco G 60), the residual fluorescence was below the Raman peak, as shown in figure 5. There is no reason to suspect that further filtration could not have reduced the fluorescence still more.

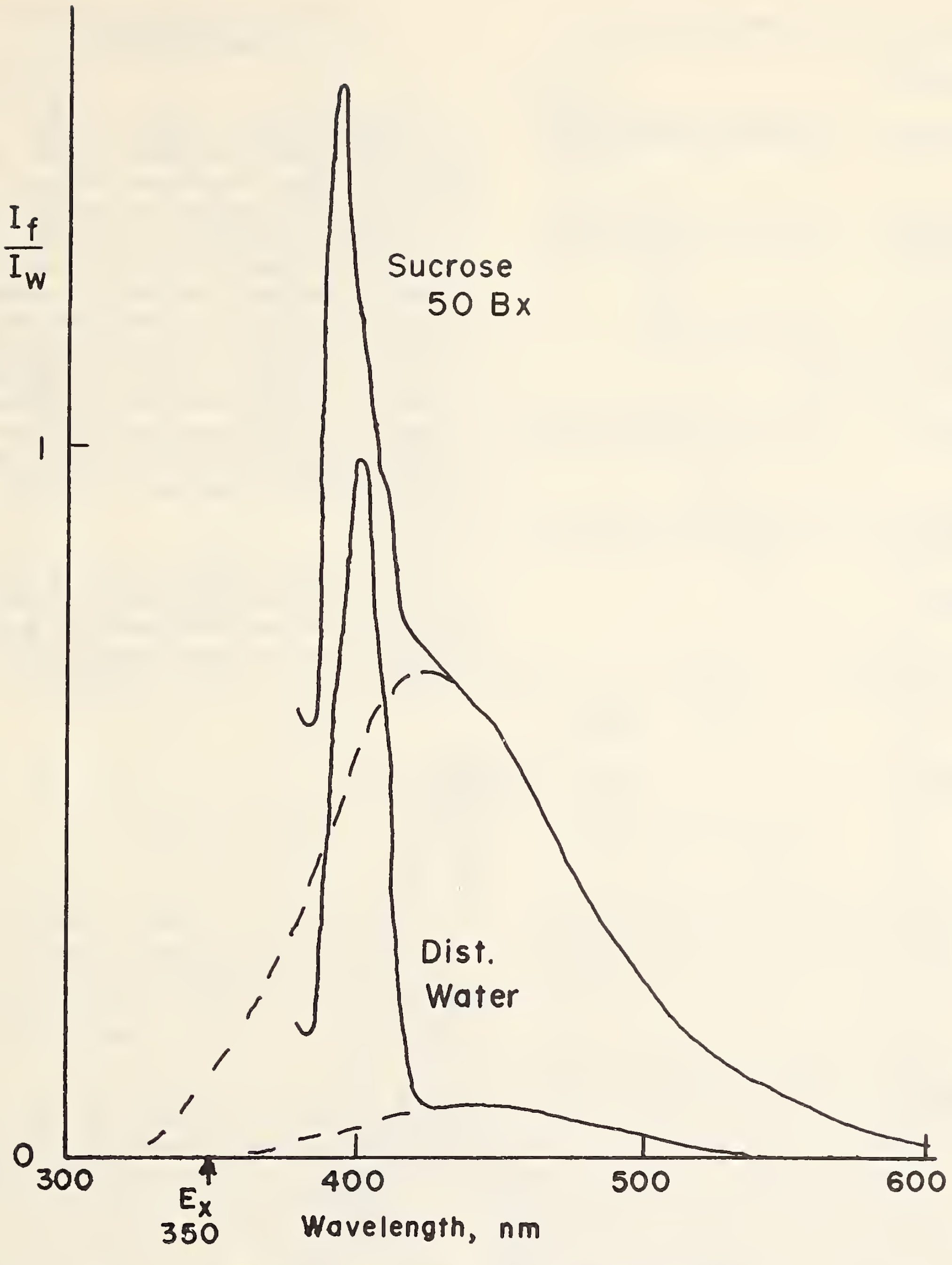

Figure 5. — Fluorescence of pure sucrose and water

This figure confirms that sucrose and water have no fluorescence and shows that distilled water introduces no contamination. The fluorescence in the sucrose is due to the residual of the constituents that we intend to use fluorescence to measure.

NOTATION FOR ORGANIC COMPOUNDS

Because of the unwieldiness of proper organic names, the following notation is introduced:

NOTATION FOR ORGANIC COMPOUNDS IN SUGAR

SUC	sucrose
QS	quinine sulfate
CLH	chlorogenic acid
CAH	caffeic acid = 3,4-dihydroxycinnamic acid

COH	p-coumaric acid = p-hydroxycinnamic acid
CIH	cinnamic acid
FEH	ferulic acid = 4-hydroxy-3-methoxycinnamic acid
SIH	sinapic acid = 4-hydroxy-3,5-dimethoxycinnamic acid
UMB	umbelliferone = 7-hydroxycoumarin
HBH	p-hydroxybenzoic acid
VNH	vanillic acid = 4-hydroxy-3-methoxybenzoic acid
SYH	syringic acid = 4-hydroxy-3,5-dimethoxybenzoic acid
FUH	fumaric acid
ACH	aconitic acid

EXCITATION AND EMISSION WAVELENGTH

Pure compounds show certain fluorescence characteristics. One of these is shown in figure 6, where the emission of UMB is given for several different excitation wavelengths. It is seen at once that the emission is at the same wavelength no matter what the excitation wavelength. This is because only one electron, some place in the molecule, is doing all the fluorescing, and this is between two definite energy levels. The excitation wavelength supplies the energy to knock the electron up to its higher energy level, and even if the excitation energy were a little more than needed, the electron would still go into the same upper energy level. A little later when the electron returns to its lower energy level, causing fluorescence, it will release always the same amount of energy (emission wavelength).

Figure 6 shows only three curves of a whole family of curves. A cross plot is shown in figure 7. The excitation curve shows the intensity of fluorescence as a function of excitation wavelength at constant

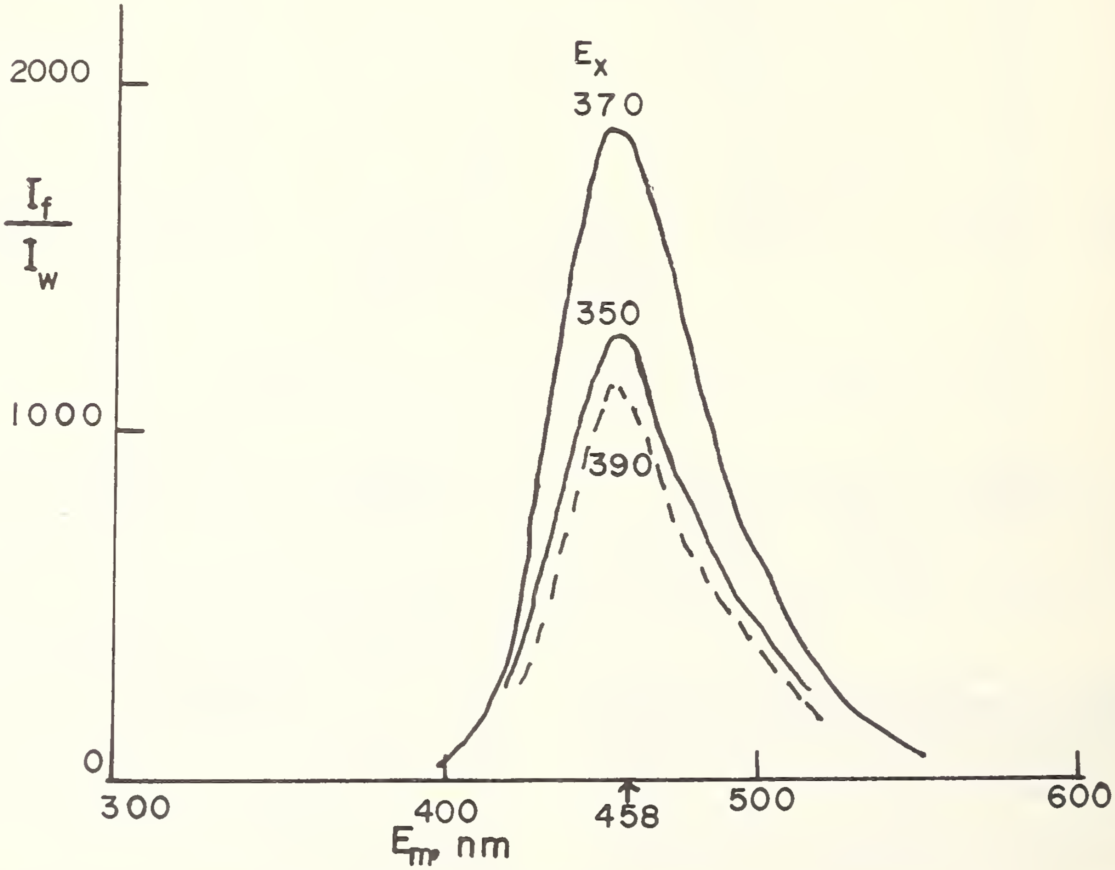

Figure 6. — Fluorescence of a pure material. UMB, 1 p.p.m., pH 10.

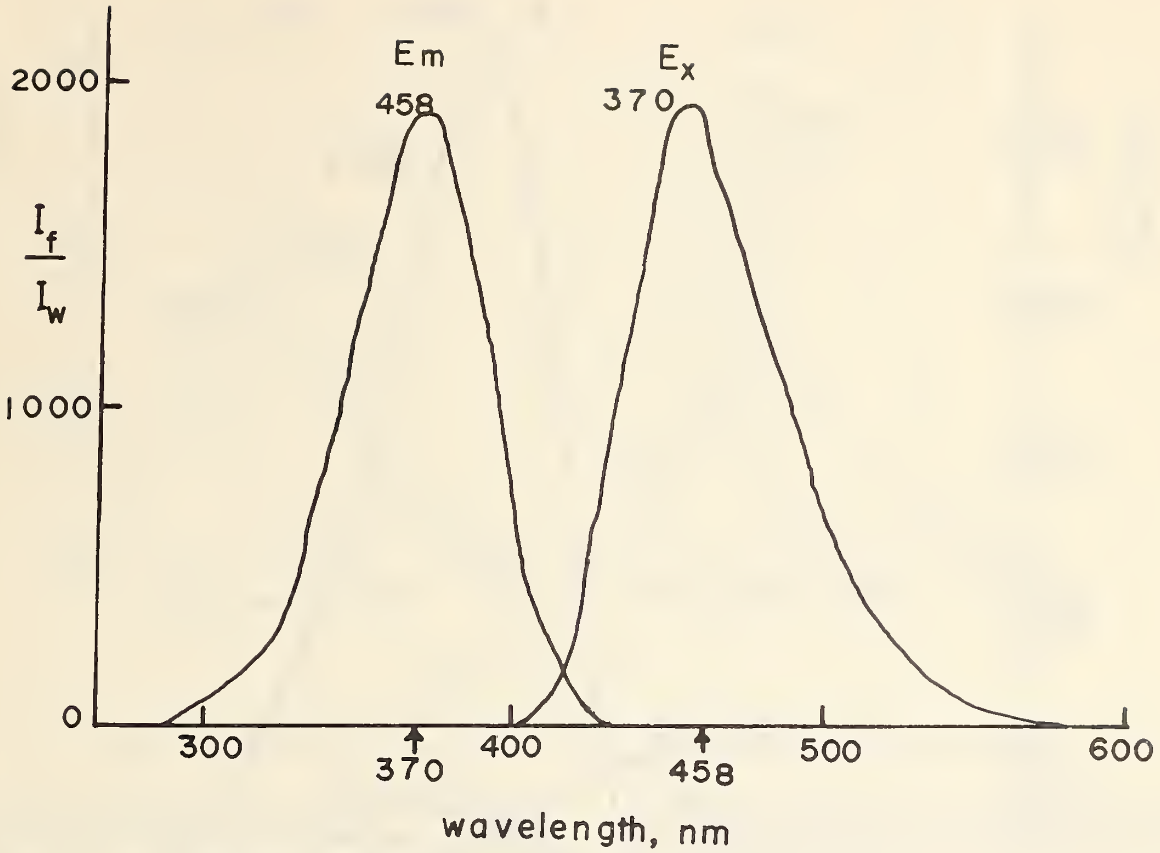

Figure 7. — Excitation and emision curves. UMB, 1 p.p.m., pH 10.

maximum emission wavelength. The emission curve shows the intensity of fluorescence as a function of emission wavelength at a constant maximum excitation wavelength. Both curves represent the same data plotted in different ways.

Equation 1 states that the fluorescence is proportional to the absorption, and the excitation curve (in figure 7, for instance) gives the fluorescence as a function of absorbed (exciting) wavelength, so this should be the absorption curve. This is found to be indeed the case for many compounds, but not all. It is possible for light to be absorbed without accompanying fluorescence, and then the absorption curves and excitation curves will differ. This will be considered further in a later section.

EFFECT OF pH ON FLUORESCENCE

pH Is well known to affect the color (light absorption) of many materials, and especially the sugar colorant. Since fluorescence can occur only after absorption, pH should affect the fluorescence, too, of those materials in which it affects the absorption. Although fluorescence is intimately connected with absorption (through equation 1), the optical effect is at another wavelength and can thus behave quite differently.

Figure 8 shows the typical effect of pH on a pure compound, CAH. The emission peak at 470 nm. is excited at 390 nm. and is very pH dependent. The change in pH changes the intensity of the peak, but does not shift it either in excitation or emission wavelength. This is because the difference in pH causes changes in the structure of the molecule and changes the relative amount that is in the form which has the electron configuration for fluorescence. Data such as these are used in proof of structure work, but that area is beyond the scope of this report.

This same molecule, CAH, has another fluorescent peak at 415 nm., excited at 330 nm., that is not pH dependent. This is an example of a molecule having two fluorescent centers, causing two fluorescence peaks. Molecules are known which have a very large number of fluorescence peaks, although usually one peak will predominate. There is no rule that an increase in pH causes an increase in fluorescence; the reverse is sometimes observed.

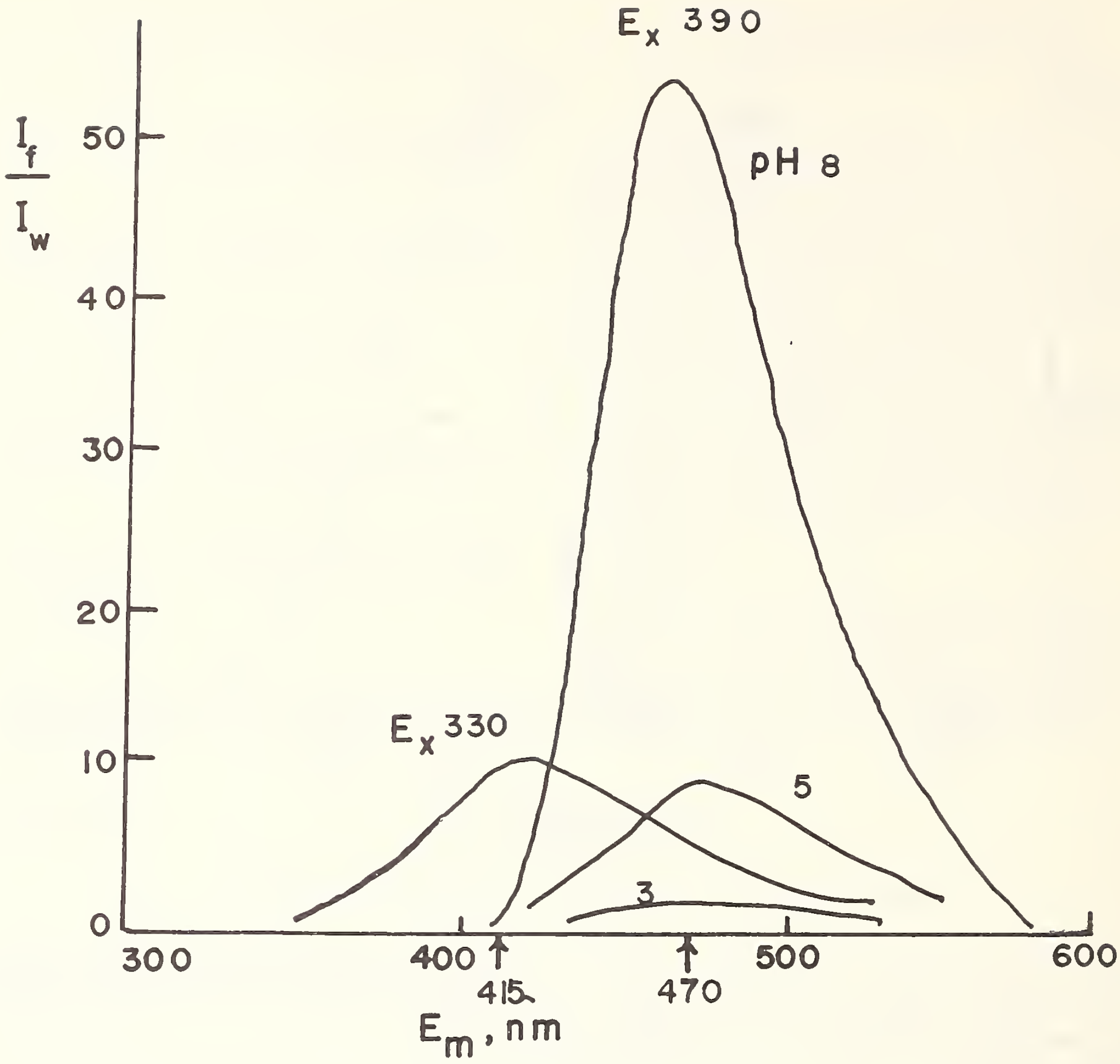

Figure 8. — Typical effect of pH. CAH, 20 p.p.m.

FLUORESCENCE IN MULTICOMPONENT MIXTURES

In a mixture of many different compounds the resulting fluorescence is the sum of the individual fluorescences. This would be expected to result in a gradual rounding off and blurring of the fine details that can be observed for individual pure compounds. The wavelength of maximum emission, instead of remaining fixed as the excitation is changed, would be expected to shift gradually as the different components of the mixture reach their peak fluorescences. Likewise, the effect of pH would be expected to result in a gradual shifting of the curve.

The sugar colorant is a prime example of a multicomponent mixture, and both of these effects are shown in figure 9 for a typical clarified washed sugar liquor. Notice that as the pH goes from 4 to 10, the maximum peak increases in intensity and occurs at a slightly lower wavelength. The peak that is excited at 330 nm. decreases in intensity and does not shift in wavelength. The peak excited at 460 nm. does not change.

The fluorescence maximum at a wavelength of about 440 nm. seems to be a property of many sugars. A change in pH seems to change the excitation maximum without shifting the emission maximum. This is probably not an inherent property of any one or several sugar colorants; it is probably a coincidence that collectively the many colorants act in this way. This is further demonstrated for an even greater change of pH with a typical raw sugar in figure 10. Here it is seen that the emission maximum does not shift in going from pH 2 to 10. This figure also shows the relation between absorption and excitation curves for sugars.

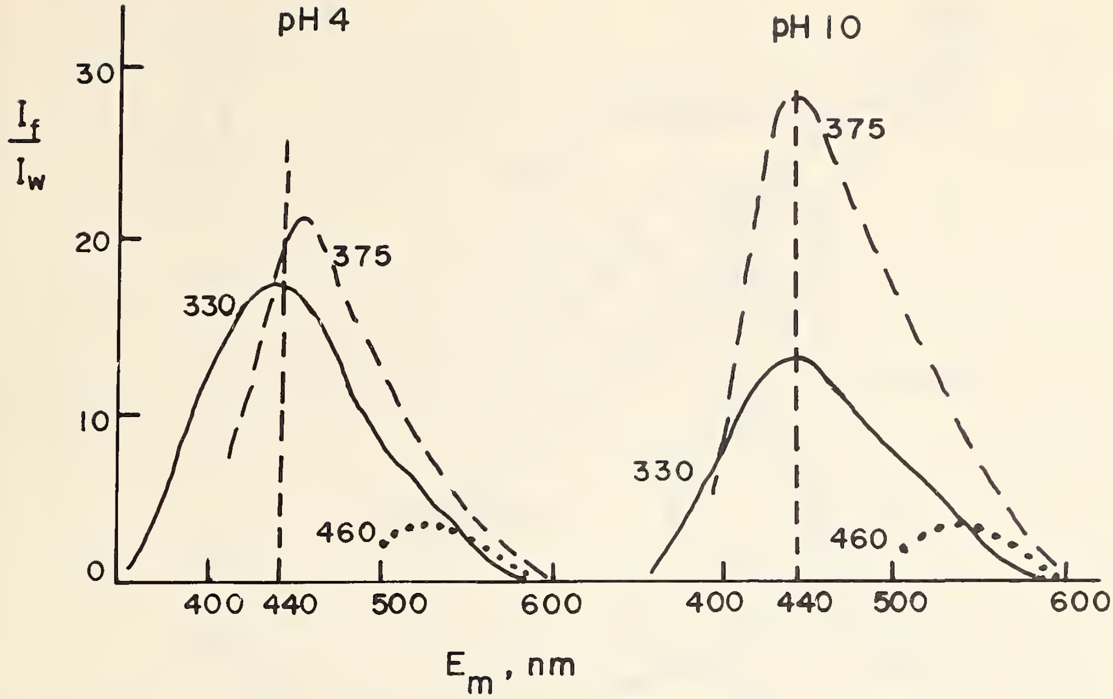

Figure 9. — Effect of pH on fluoroescence in a typical clarified washed sugar liquor. $7B_X$.

At high pH raw sugars are more colored, and the absorption curve for the high pH is higher, as would be expected. The excitation curve is not shaped at all like the absorption curve. This is not unexpected, since the raw sugar contains a great many colorants, some of which undoubtedly do not fluoresce, as mentioned previously. The excitation curve can be interpreted as the shape of the absorption curve of the components that do fluoresce. But more important, the excitation curve shows a definite shift in the wavelength of the maximum, which corresponds to the shift in wavelength of the absorption curve. This means that the pH dependent colorants are fluorescent. Also, an increase in pH shifts the absorption curve but does not raise the intensity. The fluorescence curve has peaks, the shifts and heights of which are more amenable to interpretation than the ever upward-sloping absorption curve.

These curves for sugars have shown only a few of the whole family of curves that are, of course, present in each case. A more complete family of curves for a typical sugar is shown in figure 11. Here, the gradual shifting of the height and position of the emission curve as the excitation changes is clearly in evidence. This gradual shifting makes detailed interpretation of the peaks impossible. In this particular case, a little fine structure began to appear for an excitation of 425 nm., which resulted in two definite small peaks at 450 nm These had disappeared, however, by 475 nm.

As mentioned previously, fluorescence is three-dimensional, and only two dimensions can be plotted on plane paper with the third dimension shown as a parameter. There is an alternate choice of the two dimensions to plot, which is shown in figure 12.

Here the emission wavelength is shown as a function of the excitation wavelength with intensity of fluorescence as the parameter. This is a contour chart showing in map form the shape of the fluorescence hill. This is the same data as figure 11 plotted in a different way, which may be more informative.

FLUORESCENCE OF SUGARS

Besides the three dimensions of fluorescence, the fluorescence of sugars is also dependent upon pH, which makes a total of four dimensions, or infinity to the fourth power amount of data to digest. This is an impossible task for a preliminary survey, and since pH seemed to have the same general effect on most sugars, the rest of the survey was conducted at one pH only, pH 10.

The samples of sugar or sugar products were dissolved or diluted to be within the range of the instrument. This could be judged by the color which had to be between water white and a very light yellow. The transmittance at 420 could be no less than 70 percent. The concentrations were in the range of 50° Brix for granulated sugars to 0.001° Brix for molasses. This was brought to pH 10 with NaOH and the transmission in a 1 cm. cell recorded over a range of wavelengths well into the ultraviolet. It was then placed in the fluorimeter and the emission recorded

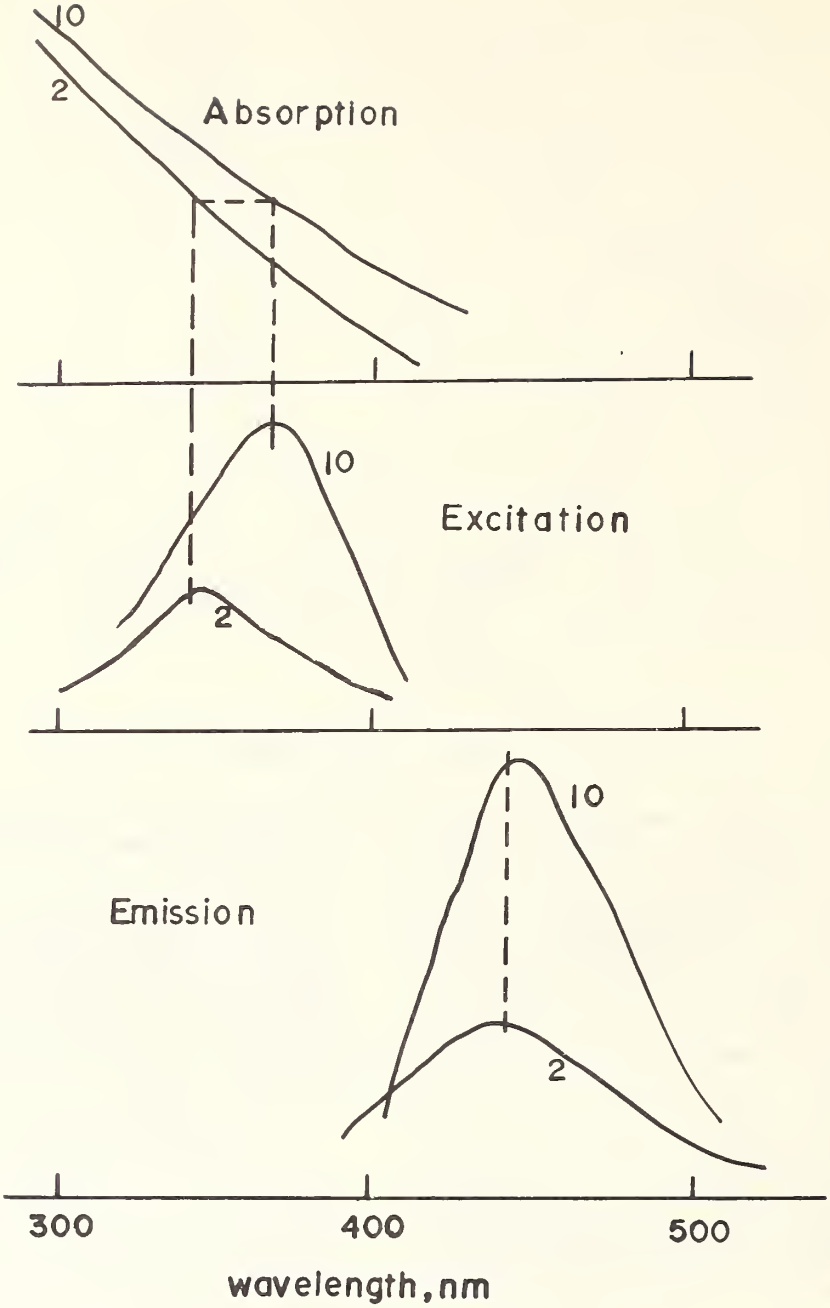

Figure 10. — Absorption and excitation curves for a typical raw sugar showing also the effect of pH.

for about six excitation wavelengths bracketing the excitation maximum. A cell containing only water was then placed in the instrument and the Raman peak of water recorded for reference purposes.

The complete recorded data were far too numerous to compile, so the summary given in table 1 was gleaned from the complete data. Usually, only the E_x, E_m, and I_f for the principal peak are given. In some cases, there was a pronounced secondary peak which was included also. The intensities of the fluorescence peak and the water peak are in arbitrary units. All other column headings are self-explanatory. The fluorescence of distilled water, purified sucrose, and quinine sulfate are given first for reference.

The next three samples were to test the constancy of I_f/I_{wc}; the test is considered affirmative. Additional corrections for transmittance of the samples of higher concentration would have resulted in a more constant value.

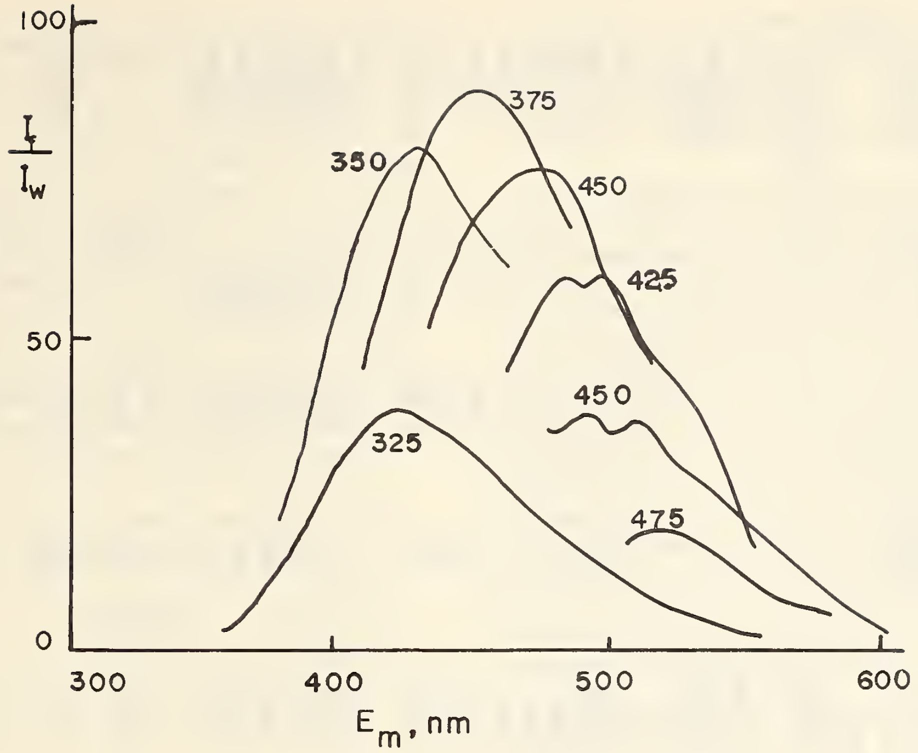

Figure 11. — Complete family of fluorescence curves for a typical sugar. La Raw, 5Bx, pH5.

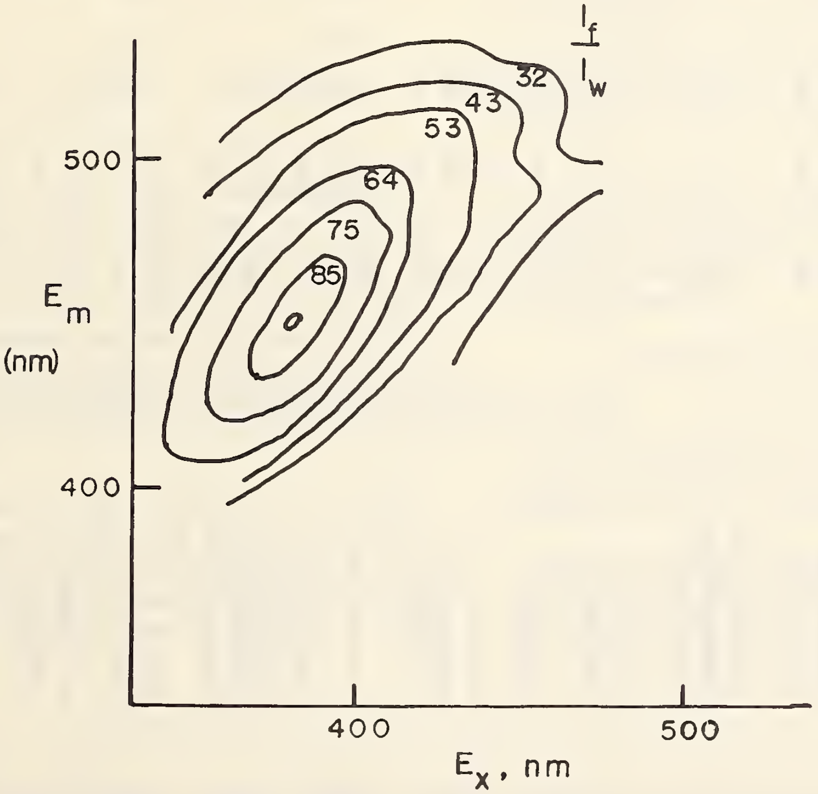

Figure 12. — Contour chart of same data as figure 11. La. Raw, 5Bx, pH5.

Table 1. — Fluorescence peaks and colors of various sugar products

Sample Number	Description	pH	E_x nm.	E_m nm.	I_f	I_w	conc. g/ml	T_{420} Percent	$-\log T$	$\frac{-\log T}{bc}$	I_f/I_wc
	Dist. water		350	450	1	20	1.0			0	.05
	Purified sucrose		350	425	33	46	.615			0	1.1
	Quinine sulfate	1	350	450	26	.23	.000001			0	100,000,000
1	Philadelphia mol.		350	430	28	.51	.000366				150,000
2	Philadelphia mol.		350	430	12	.51	.000117				200,000
3	Philadelphia mol.		350	430	14	5.	.0000118				240,000
9	So. African raw	10.5	375	435	63	6.9	.0043	92	.036	8.4	2,100
10	Florida raw	10.2	375	440	17	.68	.0048	88	.056	11.7	5,200
		10.2	375	440	78	3.4	.0048				4,800
11	Australian raw	10.2	375	463	66	3.8	.005	94	.027	5.4	3,500
		10.2	375	440	75	6.9	.005				2,200
12	Brazil raw	10.3	375	440	19	.71	.005	88	.056	11.2	5,350
13	Argentine raw	10.5	375	440	69	7.3	.0051	93	.032	6.3	1,850
14	St. James raw	10.2	375	440	32	.49	.0055	87	.060	11	11,900
15	Woodland mol.	10.2	375	460	70	25	.00001				280,000
15A		10.2	375	455	64	2.8	.0001	97	.013	130	230,000
16	Savannah mol.	10.4	375	440	65	2.7	.0001	92	.036	360	240,000
17	Greenwood mol.	10.0	375	440	75	2.5	.0001	95	.022	220	300,000
18	Chalmette mol.	10.3	375	440	64	4.3	.0001	95	.022	220	150,000
19	Pennsylvania mol.	10.2	375	440	71	3.1	.0001	94	.027	270	230,000
20	Gran, A + P	9.9	335	415	68	3.3	.615	94	.027	.044	34
22	1 strike	10.0	330	405	46	5.7	.615	93	.032	.055	13
23A	Soft, painted	9.9	375	440	28	.62	.005	88	.056	11.2	9,000
24	Soft, boiled	10.7	375	440	47	2.8	.002	90	.046	23	8,400
25A	Liq. off bone char	9.9	360	440	44	1.9	.183	92	.036	.197	127
26A	Liq. off ion exch.	10.0	350	440	43	1.5	.294	88	.056	.191	100
27A	Liq. on ion exch.	10.1	375	450	45	3.1	.082	90	.046	.56	180
28A	Clar. washed sug. liq.	10.0	375	445	45	3.0	.044	79	.102	2.3	340
29A	Melter	9.9	375	445	35	1.35	.041	69	.161	3.9	630

Samples 9 through 29A were a survey of various sugars and refinery liquors. The wavelengths of the emission maximum and excitation maximum remain nearly the same for all these samples which cover the entire gamut of commercial cane sugars. This near sameness for materials as divergent as first strike granulated and molasses is probably not due to a common fluorophore, but only fortuitous. And, fortuitous it is indeed, because this allows a simple one wavelength instrument to be used to measure intensity of fluorescence in all sugars. The intensity is the big variable, covering a ten thousand-fold range. A close examination of table 1 shows that sugars and refinery liquors of the same general class have about the same intensity of fluorescence. This allows us to abridge the table into a more readable size, as shown in table 2.

Table 2. — Summary of fluorescence and color of sugars at pH 10

	$\frac{-\log T_{420}}{bc}$	$\frac{I_f}{I_{wc}}$
1st strike	0.055	13
char liq.	.2	130
CWSL	2.3	340
melter	3.9	630
raw	8.4	2100
molasses	270	230000

Also included in table 2 are the corresponding sugar colors expressed in the usual terms of absorbancy index at 420 nm. The parallel between color and fluorescence is quite obvious. But remembering Equation 1, this is exactly what should be expected. The close correlation between color and fluorescence in sugars is perhaps better demonstrated in figure 13 where many of the data in table 1 are plotted. Note that the scale is a logarithmic one covering five orders of magnitude.

Thus, it can be stated that over a long range fluorescence correlates very well with color. For small differences, the correlation is not as good, because the two processes are not measuring exactly the same thing. There is no reason why one should be preferred over the other.

Both are merely an easy optical measure of a group of impurities. As a first approximation, they can be used interchangeably. For more detail, they should probably be used together in a complementary fashion as measures of slightly different classes of impurities.

In examining the position of the excitation and emission peaks more closely, it is noted that all the darker sugars have an excitation maximum at 375 nm. and an emission maximum at 450 nm.; as the purity of the sugar increases another peak appears. This other peak always has an excitation maximum at 330 nm., but the emission shifts from 440 down toward 400 nm. as the purity of the sugar increases. This feature is shown in figure 14 where the position of the peaks is shown using, for clarity, a scale with a compressed intensity of fluorescence. In this figure, the height of the peaks for one sugar is on a different scale from that of the next, although the relative position is correct. The height of the peaks for the same sugar at the two different excitations is to scale. The wavelength scale is repeated, so the two peaks really overlap and are not separated as drawn here.

For the purest sugar, the emission from 330 nm. excitation is higher than that from the 375 nm. excitation and at a wavelength of just above 400 nm.

For liquors off bone char, the two peaks are of about the same height, but the peak excited at 330 nm. is shifted less. For clarified washed sugar liquor the peak excited at 330 nm. is lower, and shifted very little. For less pure sugars, the peak excited at 330 nm. is so much smaller that it is tucked under the main peak from the 375 nm. excitation and is hidden.

In a survey of the effect of pH on fluorescence in sugars, the data shown in table 3 were obtained. No general trends were evident. A more thorough study of pH might produce some interesting differences between color and fluorescence.

FLUORESCENCE OF SUGAR CONSTITUENTS

The fluorescence spectra of some of the sugar constituents which have been identified in this laboratory[5] were also examined.

The various compounds were dissolved in water and measured in exactly the same way as the sugars; the results are reported in table 4. This complete table was again abridged to a more readable version.

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[5] Farber, L., and Carpenter, F. G. 1971, Identification of Sugar Colorants. These Proceedings, preceding paper, pp. 145-156.

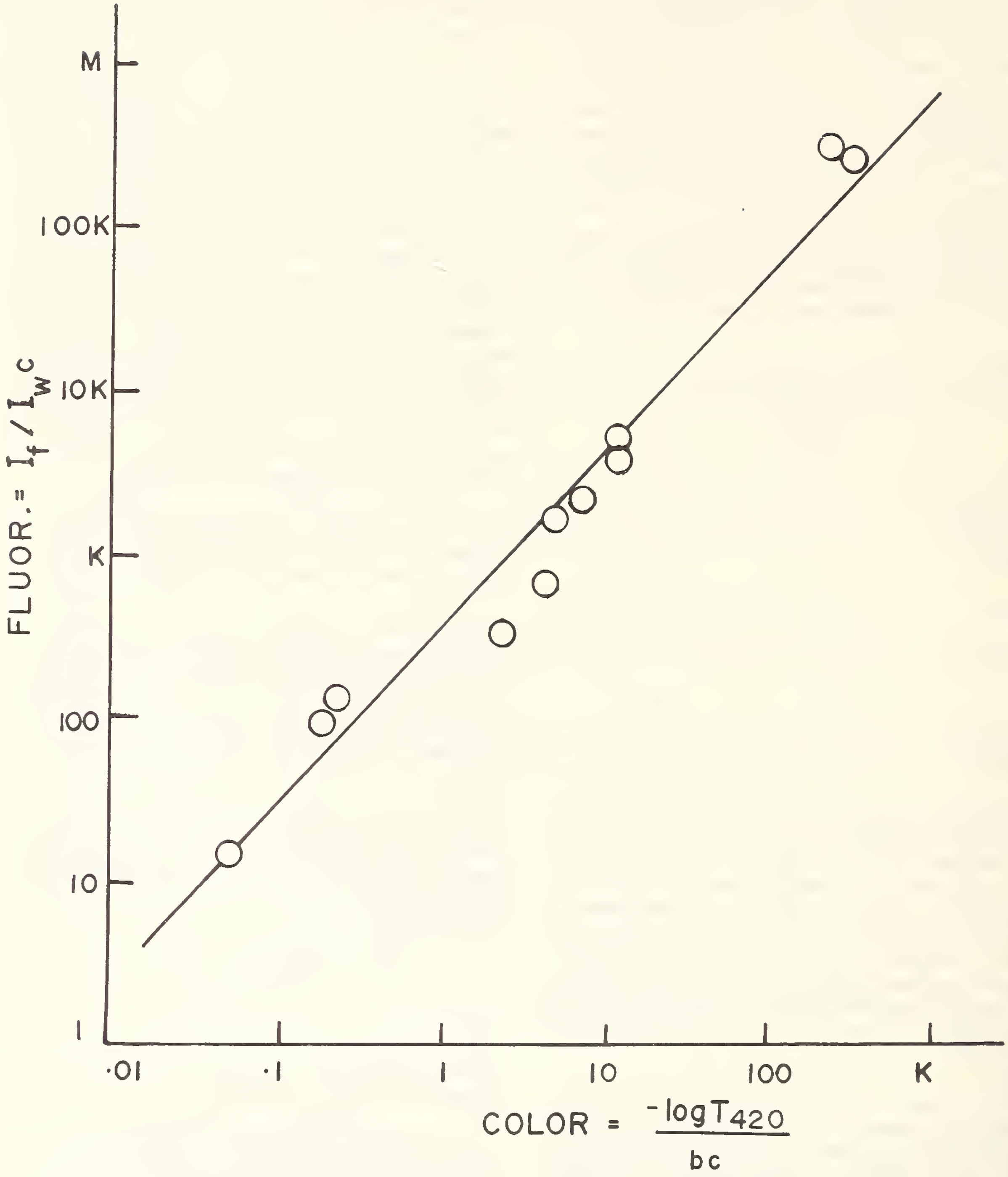


Figure 13. — Comparison of fluorescence with color for the entire range of commercial sugar products from granulated to molasses. All at pH 10.

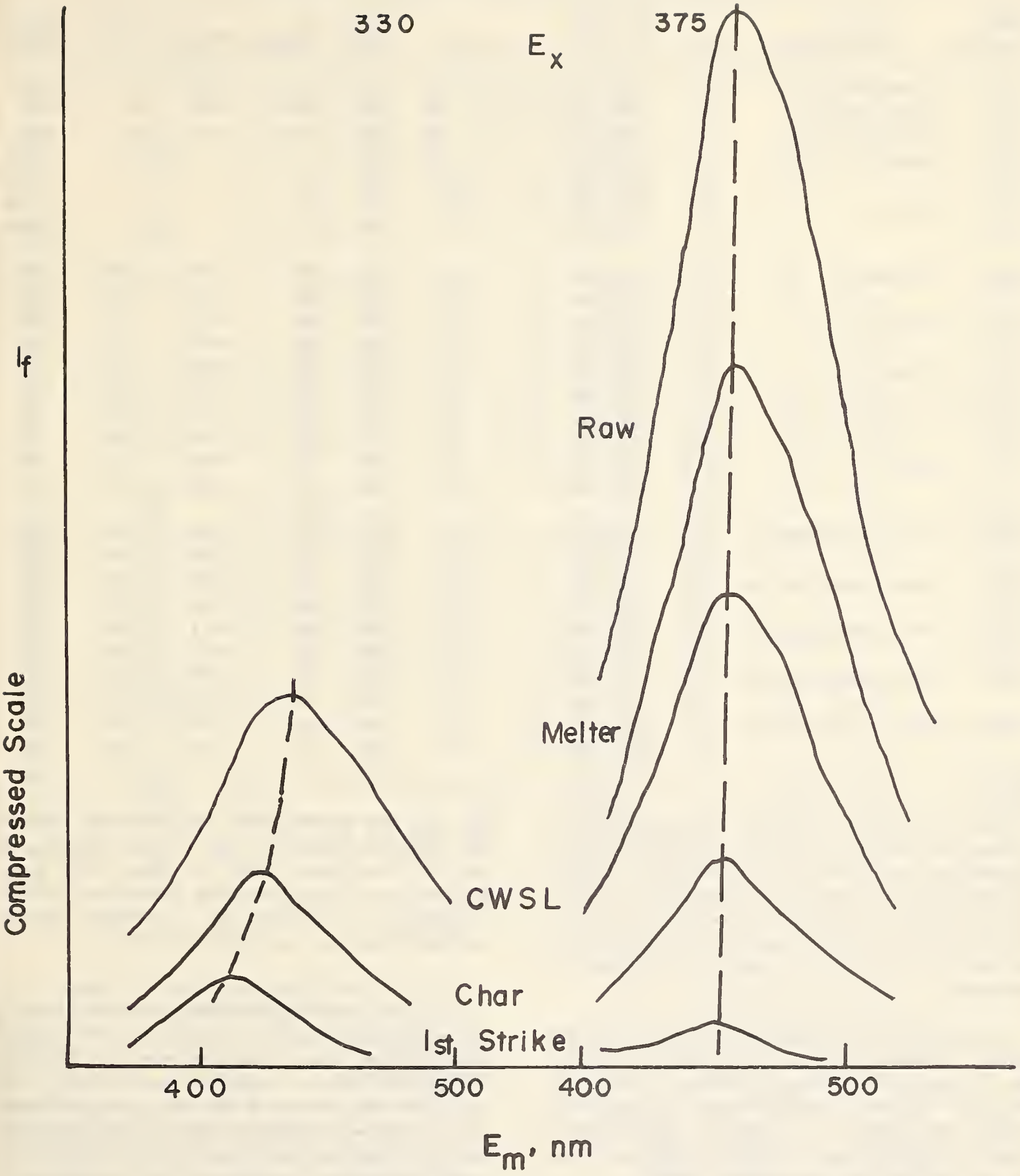


Figure 14. — General trend for emission maxima in sugars at pH 10.

Table 3. — Effect of pH on fluorescence in sugars.

Sample Number	Description	pH	E_x nm.	E_m nm.	I_f	I_w	conc. g./ml.	T_{420}	$-\log T$	$\frac{-\log T}{bc}$	I_f/I_{wc}
4	Greenwood raw	5	375	440	12.3	0.39	.005	91.7	.037	7.4	6,300
5	Greenwood raw	10	375	442	30	.50	.005	86.0	.066	13.2	12,000
6	Greenwood raw	2	350	435	13.6	.485	.005	92.5	.034	6.8	5,600
7	Gran.	2	350	435	7	.555	.615				20.5
		2	330	415	59	5.6	.615				17.1
8	Gran.	10	330	400	77	5.6	.615				22.4
		10	340	420	57	6	.615				15.4
30	Char. liq.	4.0	330	415	40	1.5	.289	95	.022	.076	92
		4.0	375	445	30	1.5	.289	95	.022	.076	69
31	Char. liq.	5.7	330	415	39	1.4	.267	94	.027	.10	104
		5.7	375	445	30	1.4	.267	94	.027	.10	80
32	Char. liq.	6.9	330	415	39	1.3	.319	92	.036	.113	94
		6.9	375	445	36	1.3	.319	92	.036	.113	87
33	Char. liq.	8.6	330	415	37	2.0	.275	90	.046	.167	67
		8.6	375	445	42	2.0	.275	90	.046	.167	76
34	Char. liq.	10.3	330	415	30	1.6	.287	87	.060	.21	65
		10.3	375	445	42	1.6	.287	87	.060	.21	87
35	Clar. washed sug. liq.	3.7	330	430	36	2.0	.072	88	.056	.78	250
		3.7	375	450	44	2.0	.072	88	.056	.78	306
36	Char. washed sug. liq.	5.7	330	430	37	1.8	.091	86	.066	.73	226
		5.7	375	450	47	1.8	.091	86	.066	.73	287
37	Char. washed sug. liq.	7.0	330	430	18	1.8	.066	85	.071	1.08	152
		7.0	375	450	25	1.8	.066	85	.071	1.08	210
38	Char. washed sug. liq.	8.8	330	430	26	1.8	.060	84	.076	1.27	241
		8.8	375	450	47	1.8	.060	84	.076	1.27	435
39	Char. washed sug. liq.	9.9	330	430	27	2.3	.062	76	.119	1.92	189
		9.9	375	450	54	2.3	.062	76	.119	1.92	380

Table 5 shows the color and fluorescence of the colored constituents. Here the correlation between fluorescence and color is seen to be strictly lacking. This indicates either that these compounds are not the major colorants in sugar, or else that the sugar colorant is made up of a very large number of compounds such as these so that, on the average, a correlation is obtained.

It is interesting that CLH, which was the first sugar colorant discovered because it fluoresced so brightly, has the weakest fluorescence per gram of matter. At the other extreme, UMB fluoresces 10,000 times brighter than CLH, yet it appears as only the faintest trace of electrophorograms of sugar colorants. It must be present in very minute quantities indeed.

Some of the recently identified constituents of cane sugar are not colored, so they should not be called colorants. Fluorescence data on these materials are shown in abridged form in table 6. They all absorb light well into the ultraviolet with no trailing off into the visible, and hence are not colored. However, as seen in the table, three of them have good fluorescence, and could be easily measured by it. This fluorescence is, however, at a distinctly shorter wavelength than the usual sugar fluorescence.

In the two other types of sugar colorants: caramels and melanoidins, individual compounds have not yet been identified. These types were examined also. The abridged data only are shown for these in table 7. All were made by inverting a 50° Brix granulated sugar solution with acid and then heating at 103° C. for the times and conditions shown in the table. The time was chosen to give only a yellow solution, not a brown or black one. Only the first reaction products were desired, not the final tar and sludge of badly mistreated sugar. It is surmised that these first reaction products might be like those produced in commercial sugar processing.

Table 4. — Fluorescence and color of some sugar constituents

Sample Number	Description	pH	E_x nm.	E_m nm.	I_f	I_w	conc. g./ml.	T_{420}	$-\log T$	$\frac{-\log T}{bc}$	I_f/I_{wc}
40	CLH	11	350	480	23	8.5	.000036	77	0.114	3200	75,000
		11	400	490	42	8.5	.000036				137,000
41	CLH	9.7	400	490	48	7	.000036	78	.108	3000	190,000
42	CLH	7.7	350	470	63	16	.000036	88	.056	1560	109,000
		7.7	400	470	52	16	.000036				90,000
43	CLH	6.3	350	460	54	15	.000036	91	.041	1140	100,000
44	CLH	3.8	350	460	38	7.5	.000036				141,000
45	CAH	3.2	345	460	45	14	.000020	93	.032	1600	161,000
46	CAH	5	330	420	33	6	.000020	90	.046	2300	275,000
		5	390	460	49	6	.000020				410,000
47	CAH	6.5	330	415	19	3	.000020	89	.051	2600	317,000
		6.5	390	465	45	3	.000020				750,000
48	CAH	7.9	390	470	53	1.1	.000020	87	.060	3000	2,400,000
49	CAH	8.9	390	470	40	.81	.000020	86	.066	3300	2,470,000
50	CAH	10.1	390	470	27	1.6	.000020	79	.102	5100	844,000
51A	FEH	10.5	360	460	40	3.7	.000005		.006	1200	2,160,000
52A	FEH	3.1	330	460	37	9.5	.000005	100	0	0	780,000
53A	COH	10.6	330	440	28	6.5	.0000005	99.5	.002	4000	8,600,000
54	COH	3.3	350	415	34	19	.000005	100	0	0	340,000
55	CIH	10.5			<1	40	.0001	100	0	0	<250
57B	SIH	11.0	350	485	47	11	.000002				2,136,000
58B	SIH	3.6	330	460	24	14	.000002	99.5	.002	1000	860,000
60A	VNH	10	312	363	62	2	.00001				3,100,000
61	ACH	10					.0001		.001	<10	<500
62	UMB	12					.0001		.31	3100	
62B	UMB	10	370	458	40	.021	.000001				2,000,000,000
63A	SYH	10	322	376	66	2.0	.00001		.001	<10	3,300,000
64A	FUH	10			<1	14	.00001		.001	<10	<500
65A	HBH	10	300	346	47	4.3	.00001		.001	<10	1,100,000

Table 5. — Fluorescence and color of some sugar colorants at pH 10

	$\frac{I_f}{I_{wc}}$	$\frac{-\log T_{420}}{bc}$
UMB	2,000,000,000	3100
COH	8,600,000	4000
CAH	2,500,000	5000
FEH	2,200,000	300
SIH	2,200,000	3000
CLH	200,000	3000

Table 6. — Fluorescence of noncolored sugar constituents at pH 10

	E_m nm.	$\frac{I_f}{I_{wc}}$
SYH	376	3,300,000
VNH	363	3,100,000
HBH	346	2,200,000
CIH		0
FUH		0
ACH		0

Table 7. — Fluorescence and color of caramels and melanoidins

		$\frac{-\log T}{bc}$	$\frac{I_f}{I_{wc}}$
Starting Invert Syrup		.015	16
pH 7.7	5 hr.	.15	62
pH 1.4	5 hr.	4.0	308
pH 9.8	1 hr.	1.7	193
1 percent asparagine in Invert			
pH 7	5 hr.	1.1	1160

The table shows that the starting invert syrup was very low in color and fluorescence. When heated at a neutral pH until slightly yellow, the color increased tenfold while the fluorescence increased only fourfold. When heated under acid conditions, the color increased 300-fold while the fluorescence increased twentyfold. When heated under basic conditions, the color increased one hundredfold while the fluorescence increased tenfold. In all these caramel-type colorants, the color increased two to ten times faster than the fluorescence, so presumably color would be a better measure of caramels.

In the melanoidin, both color and fluorescence increased at the same rate (seventyfold), so either would be a good measure of these compounds.

The entire picture of fluorescence in sugars and known sugar constituents can be advantageously presented in another way: as a plot of emission wavelength against excitation wavelength, as shown in figure 15. This becomes a form of contour chart, which is shown here without contours, with only the position of the peaks marked. The height of the peaks is not given here.

All the sugars fall within the enclosed area. All the dark sugars from molasses to raw and washed sugars fall at the same place, marked MOL. Only the more purified liquors being to move away toward the lower end of the enclosure marked GRAN. The height of this fluorescent hill is very high at the molasses end and the ridge slopes downward toward the GRAN end.

The positions of the fluorescence peaks of the various identified cane pigments and also of the caramels and melanoidin are shown all around the sugars. It is curious that only the caramels fall within the sugar band. However, it is easy to visualize how a mixture of many such colorants could have a resulting summation peak within the sugar range. The melanoidins are very near the dark sugars, suggesting that they may be a large part of the colorant in darker colored sugars. It could also be reasoned that the melanoidins are the first and most easily taken out, leaving only the caramels in lighter liquors. This same reasoning could be applied to the cane pigments, indicating that CAH and CLH are first and most easily removed and VNH, SYH, and HBH remain, pulling the remaining ridge in their direction.

COLOR AND FLUORESCENCE MEASUREMENT

It is evident that fluorescence may well become a very useful optical measurement in the sugar industry. Some comparisons with the presently used color measurement follow:

Wavelength. — Fluorescence requires two wavelengths, the color measurement only one. This complicates the fluorescence instrument but makes the fluorescence measurement more specific.
pH affects both measurements equally.
Brix, through the refractive index, affects scattering. This complicates the color measurement, but has no influence on fluorescence.
Lamp and phototube response have no effect on color but must be corrected for in fluorescence.
Color can be a correction in fluorescence and fluorescence can be a correction in color. Both are usually ignored as corrections.
Absolute values are inherently obtained in color measurements.
Fluorescence requires a Standard of reference.
The Equation expressing the color is:

$$a^* = \frac{-\log T}{bc}$$

which is complicated by the -log function. For fluorescence the equation is:

$$F = \frac{I_f}{I_{wc}},$$

which is simple and of first degree.
The Upper Limit for impure products can be extended indefinitely for both measurements by dilution.

The Lower Limit for pure sugars is reached for color when the difference between incident and transmitted beams becomes too small to measure. Commercial granulated sugars regularly reach this limit. For fluorescence the lower limit is reached when the signal from the phototube becomes obscured by electrical noise. Commercial granulated sugars are several orders of magnitude above this limit.

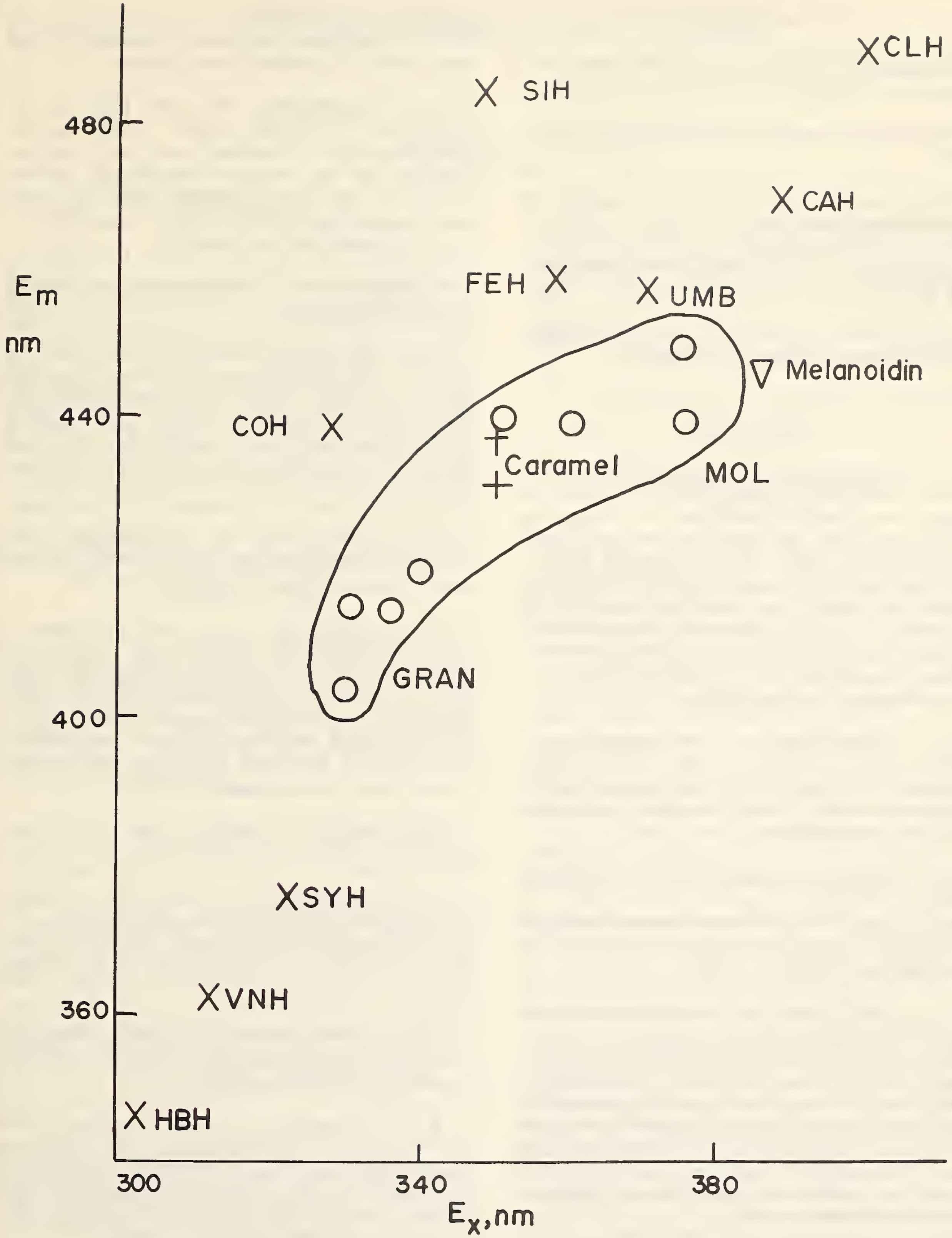


Figure 15. — Fluorescence in Sugars.

CONCLUSIONS

Fluorescence correlates well with color over a wide range and could probably be used in place of color.

Fluorescence is more sensitive than color in the low region.

Fluorescence gives peaks, which can possibly be more informative than color.

Fluorescence is a more complicated measurement to make than color.

Fluorescence shows enough promise to be worthy of further and more detailed investigation.

DISCUSSION

K. R. HANSON: One of the most dangerous occurrences in a sugar refinery is for the condensate to become contaminated with sugar. As boilers are installed with higher and higher pressures, an accident can be disastrous. There is on the market today a meter for measuring condensate which depends on fluorescence. What do you think the chances are of using this to measure leakages from an evaporator for high purity liquors with say, 3 or 4 parts per million of sugar contaminating the condensate returning to the boilers. Would the meter detect this?

F. G. CARPENTER: Yes, I would suspect that it would. A 50 Brix solution of first strike granulated sugar under U-V light fluoresces quite strongly even to the naked eye, and a sensitive instrument could easily detect lower concentrations.

K. R. HANSON: It's certainly worth investigating.

W. L. REED: Can you measure this fluorescence if the sample is in some form other than in solution — an electrophoresis paper for example?

F. G. CARPENTER: Yes. Dr. Farber's slides were all of electrophoresis paper photographed to make a cheap, convenient record. This was a photographic measure. Most of these fluorescence instruments are built so that you can put in a piece of paper at a 45° angle and measure the fluorescence right off the paper. It is a little tricky because nearly always the paper gives you background fluorescence which you've got to account for, and there is a little positioning problem, but it can very easily be done.

S. STACHENKO: There was some early work by Sandera (K., Sandera, Z. Zuckerind. cechoslovak. Rep., 51, 237 (1927), and Listy Cukrovor., 44, 569 (1925). C. A. 21-3760), and by Lunden (H. Lunden, Centr. Zuckerind., 35, 219 (1927). C. A. 21-4086), relating the U-V fluorescence technique to evaluation of beet sugar quality. Is your work related to this?

F. G. CARPENTER: This early work was on fluorescence in the visible range, and on phosphorescence. Wavelength was not measured; intensity was not measured instrumentally, but by comparison with visual standards. There was some rough attempt made, not entirely successfully, to connect intensity with ash content.

F. BRUDER: What would be the cost of a meter to measure fluorescence?

F. G. CARPENTER: There is a wide range of prices. A highly sophisticated, double monochromator instrument such as we use at the laboratory costs about $8,000. A simple U-V source costs $25.00. A simple control instrument, consisting of a source such as that, plus some color filters would cost perhaps $50 to $100.

W. L. REED: Are the electrophoresis papers sufficiently stable that they may be stored, and read with a fluorimeter after some time has passed?

F. G. CARPENTER: No, we find you cannot do this. The fluorescence changes very quickly, and cannot be stored. On occasion, it changes while you're taking a picture of it, especially with the weaker fluorescences which require exposure times up to 5 minutes; in that time, the intense ultraviolet radiation will affect the fluorescing compounds. Also, air and moisture will affect the papers, with time.

W. L. REED: You could not read any old data, then.

F. G. CARPENTER: No, that's why we take a color polaroid photograph of the paper, so that we can store our results in an unchanging form. If we tried to keep the paper, all we would have is some brown powder.

C. T. DICKERT: Would you expect a difference in fluorescence between an organic acid, its sodium salt, its iron salt, and its other forms?

F. G. CARPENTER: Yes, that's a standard method for structure determination, like ultraviolet spectroscopy. I didn't go into that phase of it at all — I just wanted to give you the practical aspects, in sugar solution. The whole subject is controversial. For example, a standard procedure is to change the pH and observe the change in fluorescence spectra, and correlate this with a suspected structure. Additional methods for structure determination are usually required.

THE EFFECT OF SOLUTION STRUCTURE ON ELECTRODE PROCESSES IN SUGAR SOLUTIONS

by

Margaret A. Clarke
Cane Sugar Refining Research Project
New Orleans, La.

ABSTRACT

Because of a history of anomalous behavior of electrodes in sugar solutions, the physical-chemical nature of the sucrose-water mixture was examined. The structure of the mixture could be explained by both the Frank-Evans iceberg and clathrate hydrate theories. Theoretical activities were calculated from the measured composition by specially developed computer programs and compared with experimental activities, found by electrodes. Both the pH and calcium electrodes, in sucrose solution, read too low at high concentrations and too high at low concentrations: explanations for these anomalies were based on structured sucrose-water complexes in the electrical double layer around the electrodes.

INTRODUCTION

In sugar refinery control operations, pH electrodes are calibrated with standard buffer solutions and then placed on stream in sugar liquor. Implicit in this manipulation is the equivalence of pH electrode response in the dilute aqueous standard buffer solutions and in the 60 Brix sugar solutions. Such equivalence may not exist.

Studies of physical processes in sugar solutions have revealed behavior different from that in aqueous solutions. Methods of pH determination are particularly affected by the change in media, e.g. pH indicators have been observed to have much narrower ranges in factory liquors than in standard buffer solutions (2). The pH of strong acid solutions with added sucrose has been found to be lower than that of the aqueous solutions without sucrose (3, 4). In similar studies, the pH's of acid sugar solutions and molasses solutions have been observed to decrease upon dilution (13, 26), whereas dilution would be expected to produce a lower concentration of acid (high pH).

Studies in this laboratory, on the calcium ion-selective electrode, have shown its behavior to differ in sucrose and in aqueous solutions. Aberrations have been observed but no satisfactory explanation to encompass them all has been proffered.

In most cases, in pH determination, and in observation of other physical properties such as solubilities, the sugar solution has been considered to be an ordinary aqueous solution with extraneous material (sugar) dissolved in it, and calculations have been based on the volume of water as the only solvent in the solution. In a first advance beyond this simple approach, the solvent is regarded as a sucrose-water mixture, which must be treated as a mixed solvent.

It is proposed that some alternatives to these simple pictures be examined, in order to explain better some of the behavior of sugar solutions.

THEORIES OF STRUCTURES OF SOLUTIONS

There are various theories about the structural state of aqueous solutions of non-electrolytes. Work is not reported in the literature on sucrose itself, but has been on polyhydric alcohols, which are a similar type of molecule having multiple OH groups.

Two principal structural concepts are relevant to sucrose solution chemistry: the Frank-Evans iceberg theory, and the clathrate hydrate theory (9).

There is considerable controversy over the existence of ice-like structures in liquid water (6, 18). Their presence is supported by such observations as the unexpectedly high heats of solution found for non-polar gases: the interspersal of the gas molecules in a highly ordered structure would require a greater amount of energy than would the process of solution in a random mixture that is assumed for simple liquids. The relatively high energetic strength of hydrogen-bonded ice-like structures accounts for the greater energy requirement observed.

Frank and Evans considered that when a non-polar molecule is dissolved in water, a microscopic "iceberg," part of a larger cluster of water molecules, would form around it, causing a loss of entropy and decreasing the total free volume of solution. This means that the dissolution of a non-polar molecule modifies the structure of water in the direction of greater crystallinity, i.e., that hydrogen-bonding is increased (7, 21). Frank and Evans suggested that non-polar molecules tend to seek out and occupy regions bordering areas where water molecules are in a more open, or more ice-like, structure and have more space.

This could stabilize the ice-like structure and thus increase the amount of solution in that form. Ice-like clusters are formed more readily, and have more stability, in regions bounded by non-polar molecules such as sucrose, because these non-polar molecules are relatively inert to the transmission of disruptive forces, such as torques, displacements, and electrostatic interactions, because of their low polarizability (5, 8).

To take another point of view (19), the greater the number of bonds associated with a water molecule (or, the higher its coordination number), the lower is the energy level of the molecule. The more clustered, or ice-like, the water molecules are, the more stable is the solution. Calculations (19), from IR spectra, on the degree of hydrogen-bonding, show (table 1) a considerable increase in degree of bonding, and hence structured order, upon the addition of a non-polar solute (hydrocarbon) to pure water.

Table 1. — Effect of "Iceberg" formation on water structure

	Pure water	With hydrocarbon
	Percent	Percent
Unbonded	29.5	21.3
Quadruply-bonded	23.3	43.0
Total number of H-bonds	46.2	59.3

In going from pure water to the hydrocarbon solution, there is a decrease in the total number of unbonded molecules, i.e. those not in clusters; an increase in the number of quadruply-bonded molecules, i.e. those of the highest coordination number, and an increase in the total number of hydrogen bonds.

The other structural theory pertinent to sucrose solutions is that of the clathrate hydrate lattice. This theory is based upon a three-dimensional lattice of solvent molecules, which is stabilized by the presence of "guest" molecules in the lattice cavities. The empty lattice cannot exist; in pure water, according to this theory, the "guest" molecules are other water molecules, not bonded in the lattice. In the water lattice, oxygen is coordinated in a slightly distorted tetrahedron, with unit cells of various types of polyhedra, with the plane pentagon as the most common surface (25).

The degree of stabilization varies with the polarizability of the "guest" molecule: the most favorable molecules are non-polar and comparatively inert. Sucrose is, therefore, a favored, stabilizing "guest" molecule.

By this theory, the high negative heats of solution found for nonpolar gases can be partly attributed to breakdown in the long range order of the water lattice, through displacement of the water "guest" molecules by the solute molecules.

Studies on various properties of dilute solutions indicate that the order of structure of water may not be decreased upon addition of a solute, although the nature of the structure may be changed. For dilute solutions of alcohols, the limiting partial molar volumes are smaller than the volumes of the pure liquid solutes at the same temperatures, thus indicating a greater ordering of structure and a lower free volume of alcohol in solution. The difference increases with increasing size of the nonpolar part of the molecule.

Formerly, before structural order in solutions became apparent, unusual behavior in solutions was ascribed to changing dielectric constant. This is now known to be an over-simplified picture. For example, when heats of solution of sodium iodide are measured (24) in various pure organic solvents and in mixtures of water and dioxane having the same dielectric constants as the pure liquids, marked differences are found for the heats of solution in any pair of isodielectric solvents.

Figure 1 compares the dielectric constants of sucrose-water solutions (17) and dioxane-water solutions (11, 20); dioxane is another nonpolar molecule. The effect of addition of sucrose to water is much less than the effect of addition of dioxane to water. The difference could be accounted for by a highly hydrogen-bonded ordered structure of sugar and water. A study comparing heats of solution of salts in sugar-water mixtures to those in isodielectric organic solvents should give further insight.

Anomalies, again in alcohol-water mixtures, in various other processes (reaction kinetics, flocculation of polymer emulsions, and acid-base properties), cannot be accounted for solely in terms of change in dielectric constant; they must be partly due to the structure of the solution.

Studies in this area of extent of structure in solution have not yet been made on sucrose solutions. Changes in the energy-volume coefficients of alcohol-water mixtures reflect the changes in their solution structure (15). Calorimetric measurements to determine partial molar heats and heat capacities have been done on some monosaccharides (including glucose, galactose and mannose) to study their interaction with water in solution (16). The effect of addition of structure breakers, such as simple electrolytes and urea, which decrease cluster-structure in water and lower the temperature of maximum density, and structure makers, or structure promoters, such as monohydric alcohols, and tetraalkylammonium salts, which have the reverse effect, has been examined for various solutes (23). Studies such as these on sucrose solutions should give information on the structure of the sucrose-water mixture, and hence possibly explain the anomalous behavior of pH and other electrodes, the solubility of sucrose and the solubility of other salts (eg. calcium phosphate) and other materials in sucrose mixtures.

It is appropriate at this point to consider the molar concentrations in concentrated sugar solutions. In the pure state, water has a molarity of 55.5. In a 60 Brix sucrose solution, the sucrose is approximately 3 M and the water 27 M. There is a ratio of one sugar molecule to nine water molecules. Since water exists in tetrahedral groups, there are approximately two of these groups to each sugar molecule. Most of the water can, therefore, be considered "bound" and the ratios are in support of a highly ordered structure of solution.

ELECTRODE PROCESSES

All analytically useful electrodes must behave according to the Nernst equation:

$$E = E^{\circ} - \frac{RT}{nF} \ln[a]$$

where: E = electrode potential

E° = standard electrode potential. $a = 1$

R = gas constant

T = absolute temperature

n = number of electrons transferred per ion. $n = 1$ for H^+

$n = 2$ for Ca^{++}

F = Faraday constant

a = activity, moles/litre

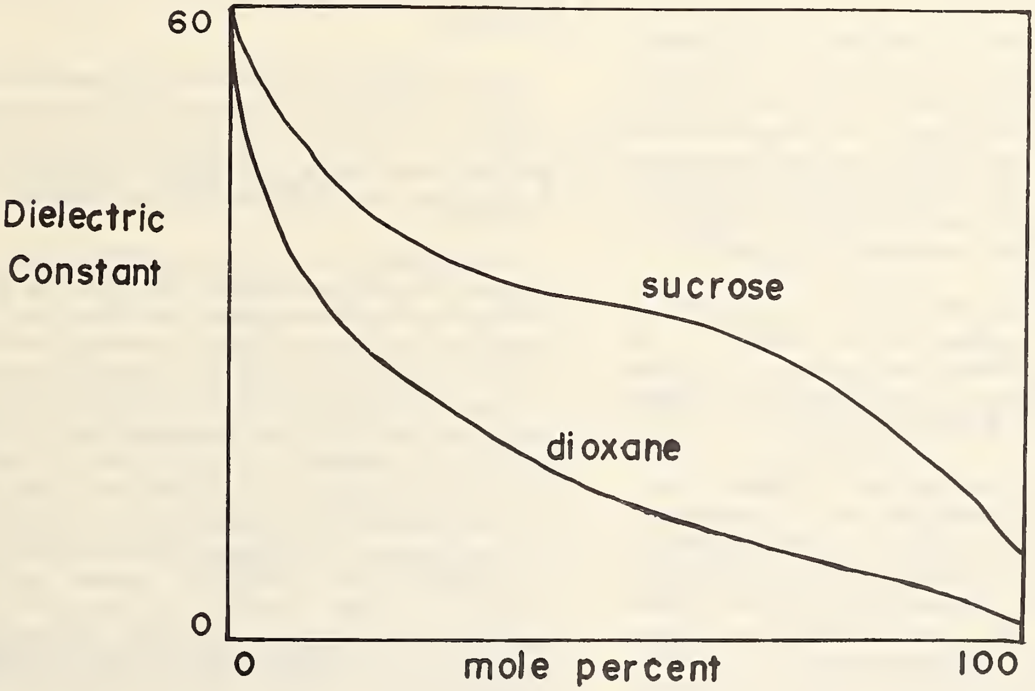


Figure 1. — Variation of dielectric constant with concentration, for sucrose and dioxane solutions.

Dielectric constant of pure water, 25°C. = 78.29
Dielectric constant of 60 Brix sucrose, 25°C. = 59.94
Dielectric constant of 60 percent b. w. dioxane, 25°C. ≅ 25

In practice the E° term is $E^{\circ\prime}$, and includes, in addition to the standard potential, all non-ideal potentials: the asymmetry potential, the liquid junction potentials, diffusion potentials, etc. Because of the variation in these potentials, electrodes must be individually calibrated (in known solutions) to determine the $E^{\circ\prime}$ term. Electrodes respond to activity, the effective concentration, not to analytical molar concentration.

When the RT/nF term is calculated, and natural logs changed to base 10 logs, the Nernst equation becomes, for a monovalent ion electrode, such as the pH electrode:

$$E = E^{\circ\prime} + 0.0591 \log [a]$$

and, for the pH electrode: $E = E^{\circ\prime} - 0.0591$ pH.

For a divalent ion electrode, such as the calcium liquid ion-exchange electrode, the equation is:

$$E = E^{\circ\prime} + 0.0296 [\log a]$$

or: $E = E^{\circ\prime} - 0.0296$ pCa

A graph of electrode potentials E, in millivolts, versus (− log [activity]), as in figure 2, will have an ideal theoretical slope (called the Nernstian slope) of −59.1 mV/ unit (log activity) for a monovalent ion, such as hydrogen, and of −29.6 mV/ unit (log activity) for a divalent ion such as calcium. The intercept of the line is the $E^{\circ\prime}$ term, and varies with conditions of measurement, and from electrode to electrode.

The usefulness and accuracy of an electrode are judged by the closeness of its response to the theoretical slope. When electrodes are in sucrose solutions, their response is not Nernstian: the slopes are considerably off the theoretical values.

The activities of the hydrogen and calcium ions in solution can be calculated from the concentrations of all the substances in solution. Many simultaneous equations involving all relevant ionic equilibria and all activity coefficients must be solved. There are available many equations for the calculation of activity coefficients. The two used here were:

the Debye-Huckel Equation,

$$-\log f_i = \frac{z^+ z^- \dfrac{A}{(TD)^{3/2}} \sqrt{\mu}}{1 - \dfrac{B}{(TD)^{1/2}} a_i \sqrt{\mu}}$$

and the Guggenheim Equation,

$$-\log f_i = \frac{z^+ z^- \dfrac{A}{(TD)^{3/2}} \sqrt{\mu}}{1 - \dfrac{B}{(TD)^{1/2}} a_i \sqrt{\mu}} - b\sqrt{\mu}$$

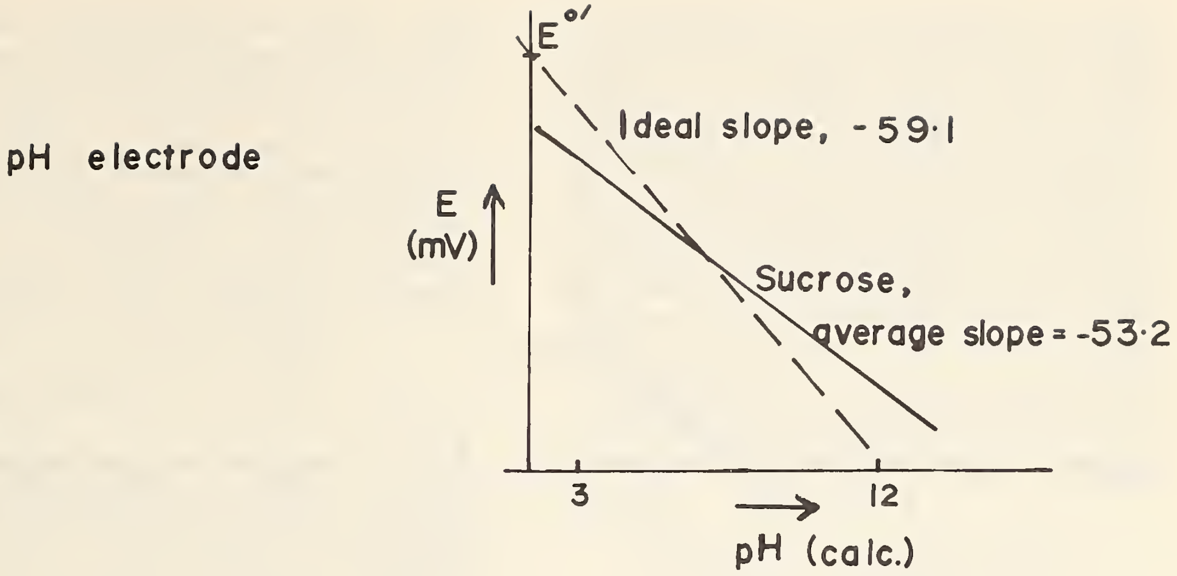
where: A and B are constants
$z^+ z^-$ are ionic charges
a_i is an ionic size parameter
T is temperature
D is dielectric constant
μ is total ionic strength
b is an ion interaction constant

Activity coefficients are determined for an ion in some particular compound, for example, Na in NaCl; hence, the ionic charges z^+ and z^- are both included in the equations. These equations have been used to evaluate single ion activity coefficients by inserting z^2 for z^+z^-, but that calculation is not theoretically sound, and a valid calculation is an item of current controversy.

This extensive calculation was programmed for a computer (CDC 1700). The output of the program was a plot of the calculated pH or pCa (the value using calculated activities) vs. mV readings, or E's, obtained experimentally, with electrodes, for each solution.

The programs were checked using aqueous solutions for both the pH and calcium electrodes; the slopes obtained in the aqueous cases were Nernstian ± 1.0 mV/pA unit. In sucrose solutions, however, the slopes were not in agreement with the theoretical, as shown in figure 2. This figure is based on data obtained from runs on six sets of 60 Brix sucrose solutions. Each set contained 12 solutions at various pH's (or pCa's). From the pH diagram, it is observed that at low pH's the experimental mV reading is lower than the calculated value i.e. the experimental pH is higher than the calculated pH value (pH increases as mV's decrease). In basic solution, at high pH's, the experimental mV reading is higher than the calculated pH value, i.e., the experimental pH is lower than the calculated value.

To express these results in another way: the pH electrode in sucrose solutions reads acid solutions at too high a pH, and basic solutions at too low a pH. From another approach, this same behavior may be observed when sugar is added to buffered acidic and basic solutions and the pH readings before and after



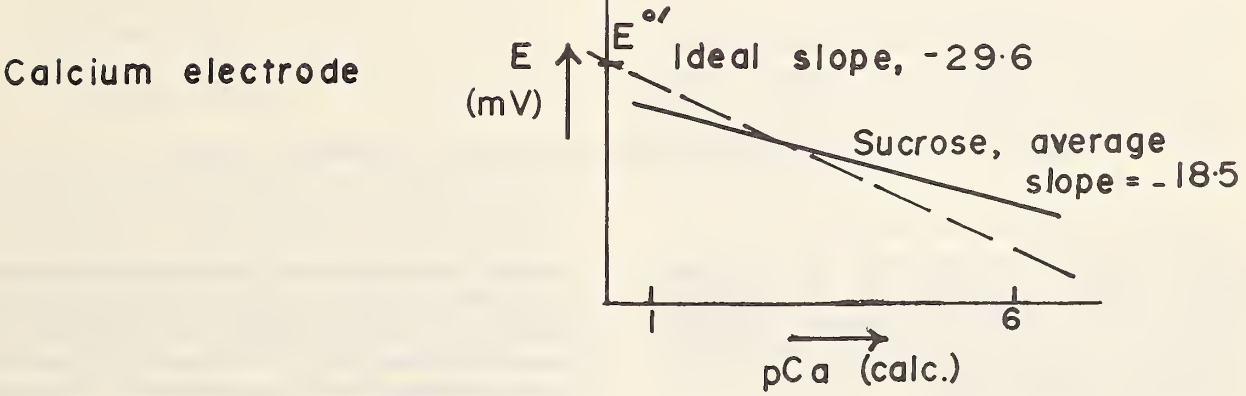


Figure 2. — Nernst diagrams for electrodes in 60 Brix sucrose solutions.

addition of sucrose are compared (fig. 3). The pH of acid solutions increases while that of basic solutions decreases. The pH of strong acid solutions changes by only a slight decrease.

These effects cannot be explained by dilution effects alone. The theoretical calculated pH takes into account the effects of dilution and volume change upon dissolution of sucrose. The remaining effects must be due to structural order in the sugar-water mixture.

Two electrode processes can be affected by this structure of solution: the liquid junction potential at the reference electrode, and the Helmholtz electrical double layer at the sensing electrode.

LIQUID JUNCTION POTENTIAL

In any electrode system where there is a liquid-liquid interface, the difference in mobilities of the ions in the two solutions sets up a potential difference across the liquid-liquid interface. This

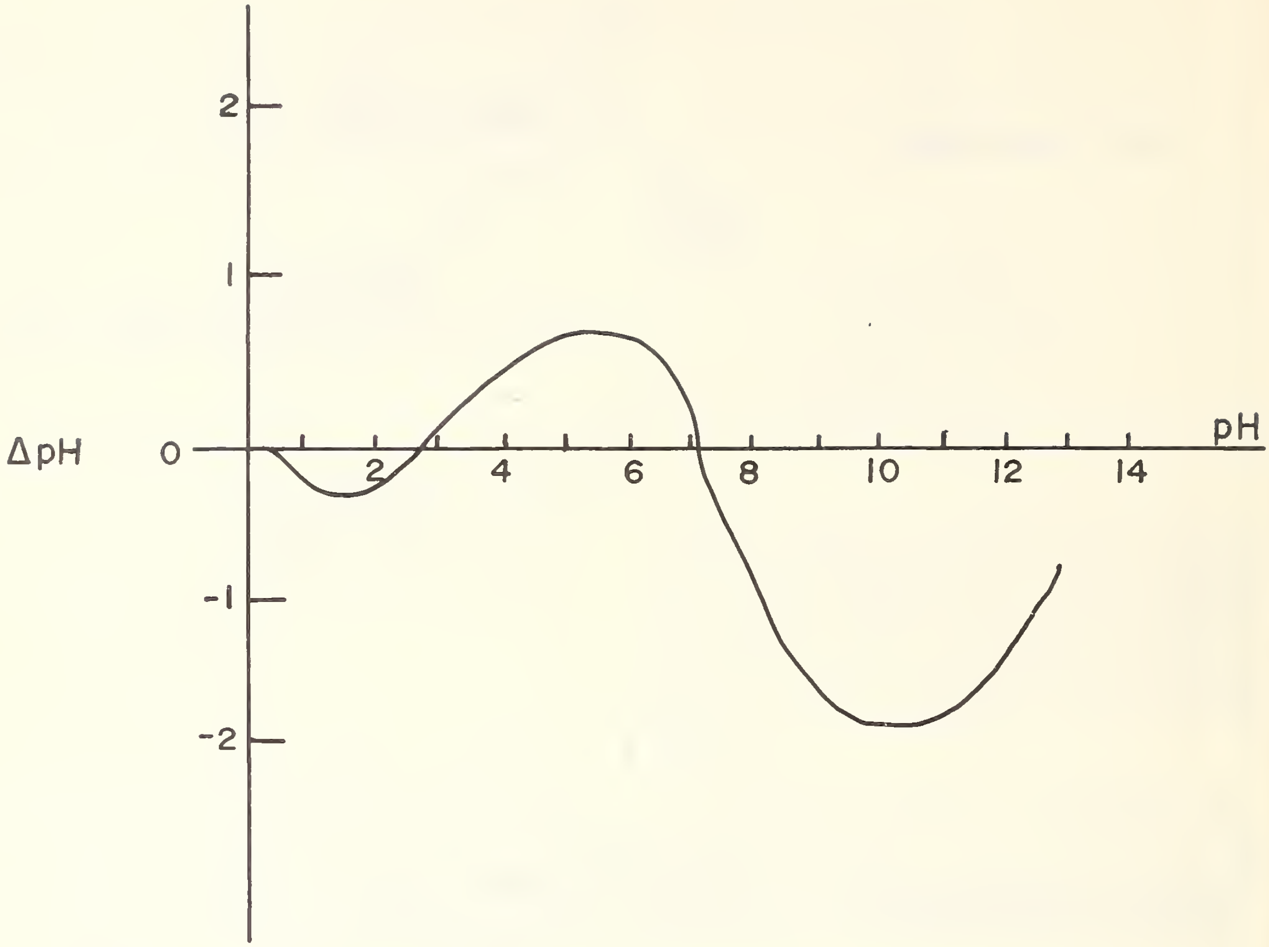


Figure 3. — ΔpH on adding sucrose to acid and base solutions. 0.1 pH unit — 6.6 mV.

potential difference is called the liquid junction potential. This potential cannot be rigorously determined; it is calculated empirically. It is a function of the activities and transference numbers of the ions on either side of the boundary:

$$E_j = \frac{-RT}{F} \int_1^2 \sum_i \frac{T_i}{z_i} \, d \ln m_i f_i$$

where 1 and 2 are the junction terminal solutions, and, for ion i:

T is a transference number

m is molarity

f is activity coefficient

and other symbols are as defined above.

This is the Henderson equation for liquid junction potentials. The liquid junction calculation cannot be experimentally determined exactly when it is based on single ion activities, for which there is as yet no thermodynamically sound experimental method of determination. In the Henderson equation, however, the potential is a function of mean ionic activity coefficients and is, therefore, determinable.

The total electrode potential of a cell, measured with a sensing electrode and a reference electrode, includes this liquid junction potential. It is in the Nernst equation in the E° term. The liquid junction potential cannot be eliminated entirely, but it can be minimized by the use of a salt bridge. This is a solution of a salt (usually KCl, because of the similar mobilities of potassium and chloride ions) which connects the electrode to the test solution. The ionic mobilities in sucrose solution, however, are not the same as they are in aqueous solution: the lowering of the dielectric constant causes a decrease in charge transference, and the sucrose-water complex structure causes a change in diffusion coefficients from values in aqueous solution. The liquid junction potentials in sucrose solutions are much greater than those in aqueous solutions: in sucrose, the range approximates 40 to 60 mV, while in aqueous solution it is only 3 to 8 mV. A familiar phenomenom in sugar chemistry is the length of time required to obtain a stable pH reading in sugar solutions, compared to the length of time in water. A lot of this delay is due to the establishment of a flowing liquid junction.

THE ELECTRICAL DOUBLE LAYER

Around the sensing electrode (glass or calcium), which is the cathode of the cell, there is a layer of cations. Surrounding this layer, to maintain electroneutrality, is a layer of anions. This construction is known as the electrical double layer, or Helmholtz double layer. The structure and behavior of the ions in this layer control the response of the sensing electrode. The double layer may be regarded as a condenser, of a potential known as the zeta potential (Z), where (16)

$$Z = \frac{4 \pi d s}{D}$$

where d = thickness of double layer

s = charge density

D= dielectric constant

The Gouy extension of the double layer concept regards the charged ions, particularly the anions, to be in a diffuse layer, a concept similar in principle to the "ion atmosphere," basic to the Debye-Huckel theory. An extended calculation of the zeta potential will have $4 \pi ds/D$ as the first term in an expansion. The extent of the diffuse anion layer varies approximately inversely with the square root of the concentration of the particular electrolyte (14). The inner layer of the cations is thought to be in a strongly oriented layer of solvent molecules, in an "ice like," but not hydrogen-bonded, array attached to the surface (12). In sucrose, the "solvent" would be the sucrose-water complex. The zeta potential is the potential between the cation-solvent layer and the bulk of solution. It is not the total potential difference between the electrode surface and the bulk of solution. Its magnitude varies with the surface potential of the electrode and the surface potential gradient. For a given surface potential, the double layer can be increasingly compressed by increasing the electrolyte concentration. Particularly effective for compression are counter anions of a higher charge.

It is possible in some instances to reverse the sign of the zeta potential, and thus affect the total potential of the sensing electrode, by increasing the electrolyte concentration, especially with electrolytes containing counter ions of higher charge; strongly adsorbed substances, such as dyes of charge opposite to that of the first (cationic) layer, often cause a reversal of sign (12). This effect is due to adsorption of more than an equivalent amount of oppositely charged material, so that a triple layer of charge is present. An examination of the effect of electrolytes upon the zeta potential of glass in electrodes (22) has shown that in this case also an increase in concentrations of electrolyte causes a decrease in zeta potential. An increase in electrolyte concentration from 1×10^{-5} M to 1×10^{-3} M will for a 1:1 electrolyte, cause a decrease of 100 mV, and for a 4:1 electrolyte, a decrease of about 300 mV in the zeta potential, and thus in the total potential of the electrode.

ELECTRICAL DOUBLE LAYER IN SUCROSE SOLUTION

The average position of the cation in the double layer depends upon two factors: (1) the electrode surface charge density and (2) the charge and radius of the cation. These factors can be regarded as competing effects.

In sucrose, if the cation is surrounded by ordered structures of sucrose and water ("sucro-hydrated"), the charge is dissipated and the effective radius of the cation is increased. The electrode will, therefore "see" and respond to a different concentration of ions from that in aqueous solution.

In order to explain the anomalous behavior of electrodes in sucrose solutions, the following postulates are proposed. At high concentrations of the ion to which the electrode responds, e.g. low pH, the increased charge dissipation, due to "sucro-hydration," causes a lower surface charge density and thus creates a lower effective concentration, so that the electrode gives a lower concentration reading. At low concentrations of the ion, e.g. high pH, the ionic size effect becomes dominant: the greater ionic size due to "sucro-hydration" creates a higher effective concentration, so that the electrode gives a high concentration reading. These conditions account for the too high pH found in acid solutions and the too low pH found in basic solutions by the pH electrode in sucrose. The effect is greater at high pH, because at low concentrations, a small percentage means a greater absolute change than at high concentrations.

The negative change in pH, shown in figure 3, occurs at pH's lower than those used for the calculations shown in figure 2. (The readings for fig. 2 were taken over a longer time, and low pH's were not used because of the high degree of inversion which occurs in that region.) It may be due to a reversal of decrease in the zeta potential at very high concentrations of hydrogen ions in the sucrose-water layer, as mentioned above. Bennett, in work on the zeta potential of particles in cane juice (1) found that, for average cane juices, the zeta potential changed sign from negative at higher pH's to positive at lower pH's between pH 3 and pH 4. This correlates with the change from a positive ΔpH at higher pH's, to a negative ΔpH at lower pH's, found with the pH electrode.

REPRODUCIBILITY OF ELECTRODE READINGS

Reproducibility of electrode readings is considerably poorer in sucrose solutions than in water solutions. A survey of the reproducibility of various types of pH and reference electrodes, in identical samples of sucrose solution, gave a root mean square value of the reproducibility as 0.07 pH units (4.2 mV). The average precision for any pH electrode in aqueous solution is 0.003 pH units (0.2 mV). The difficulty of establishing a consistent liquid junction potential, and the variations in the homogeneity of the electrical double layer are reasons for the poor reproducibility in sucrose solutions.

STANDARDIZATION

Because of the difference in electrode behavior in sucrose solutions and in aqueous solutions, it is recommended that electrodes be standardized in solutions of the same sucrose concentration as that of the samples to be tested.

SUMMARY

The Frank-Evans and clathrate hydrate theories are both found applicable to the structure of sugar-water mixtures.

The activity concept, activity coefficient calculations, and change in dielectric constant in sucrose solutions are discussed. Computer programs are developed to calculate concentrations (activities) in sucrose solutions.

The pH and calcium electrodes are found experimentally to read too low values at high concentrations and too high values at low concentrations. Explanations, based on the electrical double layer around the electrodes in the structured sucrose-water mixtures, are proposed.

There is low precision for electrodes in sucrose solutions, partly because of the difficulty in establishing a steady liquid junction potential.

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DISCUSSION

E. J. CULP: For the curves showing the different slopes correlating the theoretical with the experimental results, you said that you derived the theoretical data not from the pH determined by millivolt measurement, but from the pH that you derived by a computer. What do you feed into the computer to get the pH in cases like that?

M. A. CLARKE: You feed in the analytical molar concentrations of solutions used, and calculate activity coefficients for all ions involved, using the Debye-Huckel and the Guggenheim equations. The concentrations of sucrose and water, the changes in dielectric constant and in total ionic strength, are all accounted for in the calculations. We checked out the computer program, by using aqueous solutions of the same ions, without any sucrose, and the slope produced by the final graphs given out by the computer were the theoretical Nernstian slopes.

F. G. CARPENTER: Essentially, you calculate what the pH meter should have read. Too often people say that pH is what you read off a meter. But it isn't. The meter reads a number and you call it the pH, and that number may be very useful to you, but the pH, especially in sucrose solutions, means something different than what you read off the meter.

E. J. CULP: Well, the reason I asked the question is that if you can calculate the pH without meters then there's no point in using the pH meter for measurement.

M. A. CLARKE: You can calculate the pH if you know the exact concentrations of all the constituents of a solution. The solutions I referred to were made up with known concentrations of known constituents. In refinery syrups, you don't know all the constituents, and certainly not all their concentrations. So it would be rather difficult to calculate a pH there. It is much easier to use the number off your pH meter. But I want to emphasize that the number is not the same as the true pH, and particularly to emphasize that the variation between the two numbers is not consistent over the whole pH range.

A. VanHOOK: In the millivolt versus electrolyte concentration plots, the slope and the intercept would also depend upon the concentration of the sugar added. On a thermodynamic basis, you would expect the slope to change because there is a very intimate relationship between the activity coefficients, not only of the electrolyte that you have there, but of the sucrose, as well as of the water. The Gibbs-Duhem equation relates this on paper, but not very well in practice. Do you have any information at all about the activity of the sugar rather than that of the electrolytes.

M. A. CLARKE: When you consider a structured sugar-water complex, at different concentrations of sugar in water, that would be different degrees of structure of the sugar-water complex. This is another way of saying that the activities of the sugar and of the water are changing. So far, all my work has been only at 60° Brix; I have not used other concentrations. We plan to try others, and if what I expect to happen does occur, the difference in experimental slope from theoretical slope should increase with increasing Brix. In Dr. Pommez's paper, in figure 5, you can see this trend for the chloride electrode. One of our eventual aims in this work is to study the activity of sucrose itself.

F. G. CARPENTER: Another important point — and one of the reasons why we started this work — is that people take pH readings in sugar solution on electrodes standardized in aqueous buffer. The reference buffer solution of low ionic strength, is very dissimilar to the concentrated sucrose solution under test. The pH electrode gives you a number, but it has not been calibrated in the correct way, and hence is not really the pH.

A. VanHOOK: It would be interesting to look at the effect of addition, to sucrose solution, of strong structure breakers such as urea, and strong structure makers such as mannitol. If you looked at these in connection with your structure model it would be quite revealing, I think

M. A. CLARKE: This is the idea behind the heats of solution study which I mentioned, that we hope to carry out with structure breakers and structure makers. Urea should be expecially interesting; of all organic compounds, it behaves most like water in aqueous solution.

C. C. CHOU: In your plot of millivolts versus calculated pH, or pCa, the difference in slope from the Nernstian value could be interpreted as a fractional electron transfer, which is impossible. You did, however, have another explanation for that. Did you ever plot the millivolts versus the experimental pH?

M. A. CLARKE: Yes, you get an ideal slope, because the millivolt reading is just another way of expressing the experimental pH — you are plotting something against itself.

RESUME

by

Frank M. Chapman
West Vancouver, B.C., Canada

To sum up this whole meeting is quite an order. I am reminded of a story about a professor who had a night on the town, after which he had a large supper of old cheese and strong onions, and thereafter slept fitfully. He dreamt that he was faced with an examination paper, on which were inscribed the Ten Commandments and below them the injunction: "You should attempt not more than seven of these." Now, when I look down this list of 12 papers, I shall ask to be excused from comment on three of them.

Logically we can divide the papers into four groups. First, we have three papers dealing with adsorbents and their implied limitations. Dr. Deitz at the Naval Research Laboratory has continued the work which did so much to improve our understanding of the virtues and also the weaknesses of bone char. Perhaps one of the greatest limitations of this admirable adsorbent is the low revivification temperature to which it may safely be subjected. Improvement in this area could be a fruitful field for effort. Dr. Chou of Amstar has added to our knowledge of pore structure and his "ink bottle pore" analogy could be valuable when we consider the possibilities of working carbons or other adsorbents in unsteady state. I shall have more to say about unsteady state conditions later.

Dr. Smith of Westvaco has talked on the testing of a new carbon. This new adsorbent was run single pass, which means that at best only 50 or 60 percent of its capacity was realized and its full capacity has yet to be determined. I think that with granular carbons, problems of low pH and relatively severe inversions are not inevitable. Some refineries show invert gains of only 0.0 to 0.03 on solids, and while this compares rather poorly with bone char, where some invert loss is general, it is still quite satisfactory if the invert limits on white sugars are not too severe.

The second group of papers deals with color and its variations. These papers are perfectly complementary to the first group. To remove 80 percent of "color" is very simple and quite cheap; to remove 97 to 98 percent, as in Japan, is expensive and complicated; to remove 99.9 percent is probably prohibitively expensive. The paper by Dr. Parker of Tate & Lyle Research Centre on color removable by ion-exchange resins shows this very clearly. Dr. Anderson of Diamond Shamrock further explained the behaviour of different types of decolorizing resins. Dr. Farber's identification of several individual colorants, with his remarkable pictures, goes to the very heart of our problem, the nature of color constituents which are not removed in the refinery.

The third group of papers — by Mrs. Velasco on chromatography, Dr. Carpenter on fluorescence, and Dr. Clarke on solution chemistry — with your permission, I will not attempt to discuss.

The fourth group of papers — Dr. Pommez's on the use of the chloride electrode, Mr. Novotny's on ion exclusion, and Mr. Sullivan's on relative filterability — brings me nearer to my own sphere of refinery operations. We all have an interest in cheap methods of increasing recovery, providing that we can market the unwanted invert and organic matter in the raw materials. My personal opinion is that the simplest and cheapest way to increase yield is to do more recrystallization in the tropics, where steam and power generally are cheap. Work on the purification of sea water is an example of this approach. Steam is a good old work horse, and some countries already produce what are basically superior raw sugars.

Chloride estimation promises to be a ubiquitous and powerful tool in refinery control and I would like to observe that, in my opinion, C. and D. in Montreal, in the control of their new affination station, are already several steps ahead of the rest of the sugar world.

There have been great advances made recently in filterability. Filterability to a great extent is a matter of keeping the leaves true and straight and the cloths clean, and of eliminating what we call "starch". The introduction of monofilament synthetic filter cloths, and the "in situ" cleaning of leaves, has made ballrooms out of erstwhile crowded filter floors.

But man is never satisfied, and must always go further. I would like now to make some comments on gaps in our knowledge and on neglected areas in our technology.

In the area of phosphate clarification — I am not at all satisfied with the present state of knowledge on after-floccing. Some phosphation refineries tend to go onto absorbent at an uncomfortably low pH, and to get excessive pressure drops in the first pass through their adsorbent columns. A close study of the effects of pH, residual phosphate, etc., on pressure drop and other parameters of after-floccing is needed.

This year I have spent three or four months summarizing files on granular carbon, decolorizing resins, and bone char. One obvious conclusion is that we are still some way from making best use of these materials. A principal problem in all adsorbent work is pressure drop across the column. Many refiners, however, neglect the negative head available below their cisterns, and suffer unnecessarily low Brix and unnecessarily long transit time in consequence.

When we consider particle size, in general, fine grist adsorbents work more rapidly and more efficiently than do large grained adsorbents, because the diameter of the capillaries varies directly with the mean aperture of the adsorbent. Alternatively, the size of the capillaries can be reduced by compaction and the pros and cons of deliberate compaction should be examined. The prize may justify the necessary corrective effort in cistern design.

We need to know more about variation in resistance across 10 or 12 foot diameter columns of adsorbent. The work of H. I. Knowles, 45 years ago, showed how much could be wrong with systems now in use. There is need to compartment the false bottom of some flat floor cisterns and observe variations in rate of flow and in color removal.

Not enough work has been done on variation in temperature on the shells of adsorbent columns and the resulting effects on viscosity. The avoidance of steep gradients in viscosity has obvious advantages in efficient desweetening — and efficient desweetening carries its own reward in minimizing desorption of ash. It is obvious that once water is on the head, the filter does not know if it is running to the sewer or to the melter.

Solid adsorbents are used not only to remove color, but also to reduce odor and to reduce the concentration of floc formers. Attempts have been made to relate transit time to mean aperture and to revivification temperature, and thus to optimize the conditions for decolorization. But parameters for the removal of odor and floc formers have not been studied at all. There could be much capital at stake.

Unsteady state operation: twenty-five years ago Harold Powers lamented that we used only the outer surface of solid adsorbents, although observations on char filters indicated that the internal surfaces were to some extent accessible. A char filter is an elastic system: by cycling the pressure, liquor can be caused to spring in and out of the pores. Here are possibilities for future research.

Much progress has been made but much remains to be done. I suggest that the research efforts of the scientists have outstripped the applications by the refiners, and I would like to see Dr. Carpenter's group invited to be more active in the design and operation of refinery pilot plants. Nine or ten years ago, Tate and Lyle Refineries at Plaistow Wharf did a great deal of work on a miniature char system which took liquor off the daily stream. Several adsorbents in several batteries could be compared simultaneously, and with careful design of the experimental conditions all the work of weighing the effluents, changing the adsorbents, reading the colors, and keeping the records was done by one laboratory technician on day work.

Work of this kind should, I feel, be continued, but both planning and interpretation should be done by people who are detached from the normal problems of production.

Our primary objective must be to increase profitability. We have little control of marketing conditions but we do have the capability to reduce operating expenses by optimising and improving on unit processes. The very existence of this body, and of S.I.T., is an acknowledgement of the advantages to be gained by pooling experience and I suggest that the capability of Frank Carpenter's group is not necessarily being fully employed.

CLOSING OF THE SESSION

by

S. Stachenko
New President
Cane Sugar Refining Research Project
Montreal, P.Q., Canada

The time has come to bring an end to this most informative and interesting session. I think that we are all well aware that the success of these meetings is related to the high calibre of the papers that are given, and we wish to congratulate all the speakers for their efforts. And now, a word of thanks to those who have contributed so much to the success of this meeting.

First of all, our thanks go to Frank Carpenter, who, as usual, has done a marvelous job of putting the program together. May I also express our thanks to Revere Sugar and Amstar for playing host to all of us. Our very special gratitude goes to Bob Kelsey for the local arrangements. Everything seems to have gone without a hitch.

I would like now to announce that the next Technical Session will take place in New Orleans, November 12 and 13, 1972. I wish you all a safe trip home and hope to see you at the next session.

ATTENDANCE LIST

Alba, Arturo, Engineer, Revere Sugar Refinery, 333 Medford St., Charlestown, Mass. 02129
Ancona, Alfred J., Chief Chemist, SuCrest Corp., 280 Richards St., Brooklyn, N.Y. 11231
Anderson, Robert E., Group Leader, Diamond Shamrock Chemical Co., 1901 Spring St., Redwood City, Calif. 94064
Anhaiser, L. A., Technical Superintendent, Imperial Sugar Co., Sugar Land, Tex. 77478

Ballard, George, Senior Sugar Technologist, Revere Sugar Refinery, 333 Medford St., Charlestown, Mass. 02129
Bartolo, A. M. Vice President, Imperial Sugar Co., Sugar Land, Tex. 77478
Beder, Rusty, Maintenance Engineer, Revere Sugar Refinery, 333 Medford St., Charlestown, Mass. 02129
Bemis, W. A., Assistant to President (Retired), Revere Sugar Refinery, 333 Medford St., Charlestown, Mass. 02129
Binkley, W. W., President, The New York Sugar Trade Laboratory, Inc., 37 Warren St., New York, N.Y. 10007
Bruder, Fred, SuCrest Corp., 280 Richards St., Brooklyn, N.Y. 11231
Bush, Stanley B., Nichols Engineering and Research Corp., 150 Williams St., New York, N.Y. 10038

Chapman, Frank M., 1855 Rosebery Ave., West Vancouver, B.C., Canada
Chen, James C. P., Technical Director, Southdown Lands, Inc., P.O. Box 871, Houma, La. 70360
Chou, Chung Chi, Research Chemist, Amstar Corp., 49 South 2nd St., Brooklyn, N.Y. 11211
Clapper, Thomas W., Director of Research, Kerr-McGee Corp., Kerr-McGee Bldg., Oklahoma City, Okla. 73102
Culp, E. J., Consultant, Sawmill Hill Rd., Wells, Vt. 05774

deChazal, Jean L., Operations Manager, Amstar Corp., 1100 Key Hwy, E., Baltimore, Md. 21203
Deitz, Victor R., Naval Research Laboratory, Washington, D.C. 20390
Desmond, Frank, Assistant Chief Engineer, Revere Sugar Refinery, 333 Medford St., Charlestown, Mass. 02129
Dickert, Charles T., Rohm & Haas Co., Independence Mall West, Philadelphia, Pa. 19105
Dickery, Raymond E., Supervisor-Process Control, Corn Industrial, 1 Federal St., Yonkers, N.Y. 10702.
Dixon, Thomas A., Technical Sales Representative, Pittsburgh Activated Carbon Co. Calgon Center, P. O. Box 1346, Pittsburgh, Pa. 15230
Dobson, John G., Orion Research Inc., 11 Blackstone St., Cambridge, Mass. 02139
Dowling, Joseph F., Manager of Laboratories, Corn Industrial, 1 Federal St., Yonkers, N.Y. 10702

Formeck, Charles, Chemist, Westvaco Corp., Technical Center, Covington, Va. 24426

Gallagher, Frank, Nichols Engineering and Research Corp., 150 Williams St., New York, N. Y. 10038
Gillette, E. Dwight, Corn Industrial, 1 Federal St., Yonkers, N. Y. 10702
Goss, Dianne, Secretary, Revere Sugar Refinery, 333 Medford St., Charlestown, Mass. 02129

Hageney, G. A., Amstar Corp., 120 Wall St., New York, N. Y. 10005
Hanson, Kenneth R., Director of Research & Development, Amstar Corp., 266 Kent Ave., Brooklyn, N. Y. 11211
Hohnerlein, Otto, Chemist, Savannah Sugar Refining Corp., P. O. Box 710, Savannah, Ga. 31402

Jenkens, Lonnie P., Amstar Corp., 425 Medford St., Charlestown, Mass. 02129

Kelsey, Robert L., Revere Sugar Refinery, 333 Medford St., Charlestown, Mass. 02129

Leather, Harry, Technical Sales Advisor, Revere Sugar Refinery, 333 Medford St., Charlestown, Mass. 02129
Lebo, James E., Eastern District Manager, Westvaco Corp., 299 Park Ave., New York, N. Y. 10017
Lopez-Ona, John V., Technical Service Manager, National Sugar Refining Co., 1037 North Delaware Ave., Philadelphia, Pa. 19125
Louros, Basil G., Technical Sales Representative, Pittsburgh Activated Carbon Co., 823 N. Pennsylvania Ave., Morrisville, Pa. 19067

McConnell, G. R., Chief Chemist, St. Lawrence Sugar Refineries, Ltd., 4026 Notre Dame St. E., Montreal 4, P.Q., Canada
McGrail, T. F., Product Manager, Atlas Chemical Industries, Inc., Wilmington, Del. 19899

Mahoney, Louis E., Plant Manager, Revere Sugar Refinery, 333 Medford St., Charlestown, Mass. 02129
Meads, Philip F., Technical Director, California & Hawaiian Sugar Co., Crockett, Calif. 94525

Metzler, Joseph A., Vice President, Godchaux-Henderson Sugar Co., Inc., Reserve, La. 70084
Monroe, Frank A., Jr., President, Revere Sugar Refinery, 333 Medford St., Charlestown, Mass. 02129
Muller, E. C., Central Control Chemist, Tate & Lyle Refineries Ltd., Plaistow Wharf, London-E-16, England
Muller, George W., Jr., Supervisor-Technical Services, Kerr-McGee Chemical Corp., 1701 S. Delaware Ave., Philadelphia, Pa. 19148

Naborney, Erwin, Amstar Corp., 266 Kent Ave., Brooklyn, N. Y. 11211
Neill, Ken, Vice President-Sales, Revere Sugar Refinery, 333 Medford St., Charlestown, Mass. 02129
Nichols, J. Randall, Research Chemist, Atlas Chemical Industries, Inc., Wilmington, Del. 19899
Novotny, C. J., Industrial Filter & Pump Mfg. Co., 5900 Ogden Ave., Cicero, Ill. 60650

O'Brien, Mike, Revere Sugar Refinery, 333 Medford St., Charlestown, Mass. 02129
O'Handley, Joe, Revere Sugar Refinery, 333 Medford St., Charlestown, Mass. 02129

Pollett, Robert N., Chief Chemist, Colonial Sugar Co., Gramercy, La. 70052.
Pommez, P., Canada and Dominion Sugar Co., Ltd., P. O. Box 490, Montreal, P. Q., Canada

Ramage, James T., The Westburn Sugar Refineries Ltd., P.O. Box No. 29, Greenock, Scotland
Reed, Warren L., Chief Chemist, Revere Sugar Refinery, 333 Medford St., Charlestown, Mass. 02129
Regan, Dan, Revere Sugar Refinery, 333 Medford St., Charlestown, Mass. 02129
Rinehart, Tom M., Market Manager-Purification Chemicals, Atlas Chemical Industries, Inc., Wilmington, Del. 19899
Rosario, Tony, Revere Sugar Refinery, 333 Medford St., Charlestown, Mass. 02129
Ross, James W., Director of Research, Orion Research Inc., 11 Blackstone St., Cambridge, Mass. 02129
Rourke, Raymond A., Revere Sugar Refinery, 333 Medford St., Charlestown, Mass. 02129

Sakillaris, Mike, Revere Sugar Refinery, 333 Medford St., Charlestown, Mass. 02129
Salowey, Stanley L., Corn Industrial, 1 Federal St., Yonkers, N.Y. 10702
Schneider, Robert, Amstar Corp., 425 Medford St., Charlestown, Mass. 02129
Sciarappa, John, Amstar Corp., 425 Medford St., Charlestown, Mass. 02129
Smith, Stanton B., Westvaco Corp., Technical Center, Covington, Va. 24426
Stachenko, Stephen, Chief Chemist, Canada and Dominion Sugar Co., Ltd., P. O. Box 490, Montreal, P.Q., Canada
Steel, J. A., Jr., Chemist, Norit N.V., Postbus 1720, Amsterdam, Holland
Sullivan, John P., SuCrest Corp., 280 Richards St., Brooklyn, N.Y. 11231

Tarleton, Morris, Operations Manager, Amstar Corp., 49 South 2nd St., Brooklyn, N.Y. 11211
Taylor, Joyce A. (Mrs.), Orion Research Inc., 11 Blackstone St., Cambridge, Mass. 02129
Tippens, Dorr E., Amstar Corp., 49 South 2nd St., Brooklyn, N.Y. 11211
Tuson, W. Robert, Colonial Sugars Co., Gramercy, La. 70052
Tymann, Robert J., Revere Sugar Refinery, 333 Medford St., Charlestown, Mass. 02129

VanHook, Andrew, Professor, Department of Chemistry, College of the Holy Cross, Worcester, Mass. 01610
Velasco, V. S., Corn Industrial, 1 Federal St., Yonkers, N.Y. 10702
Villamel, A. O., National Sugar Refining Co., 1037 N. Delaware Ave., Philadelphia, Pa. 19125
Voegtlin, R. E., Vice President, Revere Sugar Refinery, 333 Medford St., Charleston, Mass. 02129

Wallenstein, Howard, Process Manager, Corn Industrial, 1 Federal St., Yonkers, N.Y. 10702
Williams, F. M., Pittsburgh Activated Carbon Co., Calgon Center, P. O. Box 1346, Pittsburgh, Pa. 15230

Zievers, James F., Vice President, Industrial Filter & Pump Mfg. Co., 5900 Ogden Ave., Cicero, Ill. 60650

PERSONNEL WITH THE CANE SUGAR REFINING RESEARCH PROJECT LOCATED AT SOUTHERN MARKETING AND NUTRITION RESEARCH DIVISION

Carpenter, Frank G., Project Leader-Food Crops Laboratory
Clarke, Margaret A., Food Crops Laboratory

Farber, Leon, Food Crops Laboratory

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